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ON

FIELD INVESTIGATION OF SULFUR DIOXIDE WASHOUT FROM THE PLUME OF A LARGE COAL-FIRED POWER PLANT BY NATURAL PRECIPITATION

J. M. Hales, J. M. Thorp and M. A. Wolf

TO

ENVIRONMENTAL PROTECTION AGENCY
AIR POLLUTION CONTROL OFFICE

CONTRACT NO. CPA 22-69-150

MARCH 1971

ATMOSPHERIC SCIENCES DEPARTMENT
BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON 99352

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FOREWORD

This report was prepared by Battelle-Northwest, Richland, Washington pursuant to Contract No. CPA 22-69-150 with the Air Pollution Control Office, Environmental Protection Agency. The Project Officer was Mr. Charles R. Hosler, Division of Meteorology.

The research which is reported was conducted by scientific and technical personnel of the Atmospheric Sciences Department of Battelle-Northwest. Mr. M. A. Wolf was the Project Director and the principal investigators were Dr. J. M. Hales and Mr. J. M. Thorp. Battelle-Northwest personnel who contributed to the investigation were:

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R. E. Wheeler

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16. Abstracts - An experimental investigation was conducted to measure the sulfur dioxide washout by natural precipitation from the plume of a large, coal-fired plant. The field investigation extended over three one-month periods in the vicinity of the Keystone Generation Station where 11 to 23 tons of sulfur dioxide, depending on power output, were released hourly from two 800 feet stacks. During rain episodes in October - November 1969 and April - May 1970, and during snowfall in February 1970, there was a total of 22 experimental runs. Precipitation samplers were placed at intervals of 4° to 12° on sampling lines encircling the keystone station at nominal distances of 1-1/4, 2-1/2, and 4 miles. Chemical analyses were performed in a mobile field laboratory. The primary objective of this study was to assess the effectiveness of precipitation washout as a mechanism for removing sulfur compounds from the plume of the keystone plant. A secondary objective of the study was to evaluate the relative importance of various interractions and atmospheric variables.

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Coal
Electric power generation
Sulfur dioxide
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Precipitation (meteorology)
Solubility
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NOMENCLATURE

a	Raindrop radius, ℓ
c	Concentration (subscripted) moles/ℓ^3
C_a	Space-curve notation
D	Diffusion coefficient (subscripted) ℓ^2/t
E	Washout efficiency, dimensionless
f	Probability-density function for drops in space, $1/\ell$
f^*	Probability-density function for drops falling through a horizontal surface, $1/\ell$
g	Function denoting equilibrium relationship, arbitrary units depending upon concentration units chosen
H, H'	Henry's-law constants, dimensionless and ℓ^3/mole respectively
k	"Film" mass-transfer coefficient (subscripted). k_y denotes gas-phase coefficient, k_x denotes liquid-phase coefficient; moles/$\ell^2 t$
K_y	Overall mass-transfer coefficient based on gas-phase driving force, moles/$\ell^2 t$
K_1, K_2, K_1', K_2'	Equilibrium constants defined by (3.28), (3.29), (3.33), and (3.34). Units vary depending upon defining equation.
m	Mass-concentration of particulate, m/ℓ^3, or total mass of particulate, m
N_o	Total number of raindrops in a unit volume of space, number/ℓ^3
N_T	Total number of raindrops falling through a unit area per unit time, number/$\ell^2 t$
r	Radial position coordinate, ℓ
$\bar{r}$	Position vector, ℓ
Re	Reynolds number of falling drop, dimensionless
Sc	Schmidt number, dimensionless

Sh	Sherwood number of falling drop, dimensionless
t	Time coordinate, t
$\bar{u}$	Wind velocity vector, ℓ/t
$\bar{v}_a$	Raindrop velocity vector, ℓ/t
v_t	Terminal fall velocity of drop, $\frac{dz}{dt}$, ℓ/t
w	Molar removal rate of pollutant by washout from a unit volume in space, moles/ℓ^3t
x	Downwind position coordinate, ℓ. Also liquid-phase mass fraction (subscripted), dimensionless
y	Crosswind position coordinate, ℓ. Also gas-phase mass fraction (subscripted), dimensionless
z	Vertical position coordinate, ℓ.
Z	Amount of pollutant carried to ground per unit area-unit time, moles/ℓ t
α	Linearized overall mass-transfer coefficient, moles/ℓ^2t
ΔY	Spacing between collectors, ℓ
ξ_a	Amount of pollutant delivered to ground by a radius - a raindrop, moles
ν	Kinemetic viscosity, ℓ^2/t

SUBSCRIPTS

A	Denotes "species A"
aq	Denotes aqueous condition
b	Denotes bulk mixture
e	Denotes equilibrium condition
E	Denotes "effective"
i	Denotes initial condition

o	Denotes interface, or ground-level depending on application
x	Denotes liquid-phase
y	Denotes gas-phase

SUMMARY

An experimental investigation was conducted in western Pennsylvania to measure the sulfur dioxide washout by natural precipitation from the plume of a large, coal-fired power plant. This information is necessary in assessing the extent of depletion from the diffusing plume and in evaluating the possible consequences arising from deposition at the surface.

The field investigation extended over three one-month periods in the vicinity of the Keystone Generating Station where 11 to 23 tons of sulfur dioxide, depending on power output, were released hourly from two 800 ft stacks. During rain episodes in October-November, 1969 and April-May, 1970, and during snowfall in February, 1970 there was a total of 22 experimental runs.

Precipitation samplers were placed at intervals of 4° to 12° on sampling lines encircling the Keystone Station at nominal distances of 1-1/4, 2-1/2, and 4 miles. The samplers were waste cans with approximately one square-foot collection area. A plastic funnel with an attached bottle was fitted to the waste can for rain collection, while a plastic bag liner was used for snow collection. A solution of tetrachloromercurate (TCM) was contained in the rain collector bottle to prevent sulfur dioxide loss. The TCM solution was omitted from the snow collectors on the basis that low, ambient air temperatures would inhibit loss.

Chemical analyses were performed in a mobile field laboratory. The sulfur dioxide analysis employed the sulfamic acid variation of the West and Gaeke method. Use of the Technicon Autoanalyzer permitted rapid assay of samples containing as little as 0.1 micromole per liter of sulfur dioxide. Analyses for pH, sulfate and nitrogen compounds were performed on selected samples.

Early experimental observations revealed that sulfur dioxide washout was

much less than predicted by preexisting theory. A revised theory was developed which incorporates the physicochemical phenomena of absorption-desorption reversibility and pH limited solubility of sulfur dioxide. The basis of the revised theory is the expression of the sulfur dioxide flux from a falling drop as

$$N_A = - K_y(y_{Ab} - g(c_{Avg})) \frac{\text{moles}}{\text{cm}^2\text{sec}} \tag{1}$$

(reversible process)

rather than as

$$N_A = - k_y\, y_{Ab} \frac{\text{moles}}{\text{cm}^2\text{sec}} \tag{2}$$

(irreversible process)

which had been employed in the previous theory. Here y_{Ab} is the mole-fraction of sulfur dioxide in the gas surrounding the drop, c_{Avg} is the average sulfur dioxide concentration in the drop, g denotes a solubility equilibrium relationship, and K_y and k_y are overall and gas film mass-transfer coefficients, respectively. It should be noted that the essential feature of Equation 1 is the parenthetic term which may be positive or negative, thereby enabling the treatment of both absorption and desorption; obviously this quality is not satisfied by Equation 2.

Elaboration and extension of Equation 1 demonstrate that for the conditions of the Keystone study a great majority of sulfur dioxide absorbed by the precipitation during its passage through the plume should be released before it reaches the ground. Additionally, this theoretical treatment indicates more effective washout from low-elevation sources and significant washout from tall stacks only at greater distances.

A particularly interesting aspect is the influence of pH on sulfur dioxide washout. The reversible theory combined with solubility estimates indicates that washout should vary strongly with pH over the range of levels observed in the field. Thus, acid-forming air pollutants sorbed by the precipitation will tend to inhibit sulfur dioxide washout.

A further result of the theoretical analysis is that sulfur dioxide washout through its capture by condensation droplets in the plume is an unimportant mechanism compared to gas-phase washout. Based on a supporting field experiment and laboratory work by others, sulfur dioxide washout through the mechanism of prior absorption on plume particulate is expected to be insignificant.

The significant results of the experimental study, which are in agreement with the revised theory, are:

1. Washout of sulfur dioxide was up to two orders of magnitude less than predicted by preexisting theory. No significant difference was observed between washout fluxes in rain and snowfall; both were clustered about a value of 10 μmoles $(m^2 hr)^{-1}$ for precipitation rate normalized to 1 mm hr^{-1}.

2. The observed relationship between washout and precipitation rate differed by a factor of two from the relationship derived from preexisting theory. The larger exponent of precipitation rate in the observed relationship with washout is interpreted as more efficient washout by large drops than is predicted by preexisting theory.

3. Washout concentrations of sulfur dioxide appeared to increase with distance from the stacks. Preexisting theory predicts concentrations proportional to the vertically-integrated mass of sulfur dioxide which should decrease with distance because of lateral diffusion of the plume.

4. Washout of background sulfur dioxide appeared to cause an inordinately strong interference with plume-washout observations. Remote sources such as the Homer City Generating Station and the Lucerne coke ovens, both about 12 miles southeast of the Keystone Station, contributed heavily to the sulfur dioxide washout.

5. Under certain circumstances, when the washout of background sulfur dioxide was relatively high, a depression of sulfur dioxide concentration was observed in precipitation collected beneath the plume. This indicated that sulfur dioxide washout was inhibited in some way by the Keystone Station or that it was converted to sulfate.

Comparison of sub-plume samples with adjacent ones, which were assumed representative of the background, showed a higher sulfate washout beneath the plume. Analysis of these cases indicates that this is not a simple conversion from sulfur dioxide to sulfate. Calculation of the degree of oxidation required to produce the observed sulfate washout flux showed that previously observed oxidation rates could account for most of the observed values. The highest values, which occurred in snowfall, are attributed to high oxidation rates and enhanced washout of larger aerosols resulting from condensation of plume water vapor on the sulfate particles. The sulfate washout flux beneath the plume in snowfall was observed to be proportional to the square of precipitation rate.

By virtue of physicochemical aspects of sulfur dioxide washout, the maximum concentration in precipitation incident on the ground apparently is reduced through elevation of the source by tall stacks. However, sulfate washout which may account for greater sulfur removal than sulfur dioxide washout in the vicinity of the source is unaffected by the increased height of emission. At greater distances, as the plume diffuses toward the ground total washout of sulfur dioxide is expected to increase and to dominate the sulfur washout processes. Definition of the resulting washout distribution remains to be determined.

CHAPTER I

INTRODUCTION

This report describes an investigation of precipitation washout of sulfur compounds from the plume of a large coal-fired, electrical generating plant. Such considerations are particularly important at the present time because of the increasing national demand for electrical power, which has been met in part by the advent of large, mine-mouth generating stations.

Such operations, by virtue of the enormous quantities of coal they consume, add considerably to the pollution load of the atmosphere. Sulfur-compound emissions, which arise from the combustion of sulfur impurities in the coal, are of particular concern in this respect. The most reliable estimates indicate that about 40 percent of sulfur-compound emissions from human activities arise from coal-fired generating facilities.(1) In the three years between 1963 and 1966, the rise in sulfur-compound emissions from coal-fired power plants amounted to roughly 2.3 million tons per year (computed as sulfur dioxide) or an increase of 25 percent.

Assessment of the effects of such increases must necessarily consider the sources, sinks, and dispersion of sulfur compounds as they relate to their physical and physiological influences on the environment. To accomplish this, the Air Pollution Control Office (APCO) initiated the Large Power Plant Effluent Study (LAPPES). The precipitation washout study described in the present report is one facet of the overall LAPPES program.

The LAPPES program is being conducted in western Pennsylvania in the vicinity of the Keystone (1800 megawatts), the Homer City (1280 megawatts), and the Conemaugh (1800 megawatts) Generating Stations. The precipitation washout study reported in this document was confined to the vicinity of the Keystone plant, although the emission from Homer City was tentatively identified as a background source.

PRELIMINARY ASSESSMENT OF PROBLEM

Upon emission of the plume to the atmosphere, the sulfur compounds that it contains are subject to a wide variety of physical interactions. Intuitively one might expect a given plume component, say a sulfur dioxide molecule, to interact with its environment in a number of ways prior to its ultimate deposition on the earth's surface. Such interactions may be represented as in Figure 1.1. This chart is incomplete in that it does not include some of the interactions that have been considered to be relatively insignificant (e.g., formation of elemental sulfur by sulfur dioxide reduction); the figure is adequate, however, in describing qualitatively the more important interactions and in lending perspective to the overall removal process. It is important to note that although the present study is concerned primarily with assessing net deposition rates (steps 4-10 and 7-8, on Figure 1.1) these ultimate processes depend upon and reflect all of the previous interactions.

It is obvious that the mechanisms depicted in Figure 1.1 will be influenced markedly by atmospheric conditions. The factors considered to be most significant in this respect are listed in Table 1.1. Visualizing a superposition of the atmospheric factors of Table 1.1 upon the physicochemical interactions of Figure 1.1 gives some indication of the complexity of the processes resulting in the ultimate deposition of pollutant material.

STUDY OBJECTIVES

The primary objective of this study was to assess the effectiveness of precipitation washout as a mechanism for removing sulfur compounds from the plume of the Keystone plant. This assessment is necessary to evaluate the significance of washout relative to increasing the delivery of pollutants to the earth's surface, and to decreasing the burden of sulfur compounds in the atmosphere. A secondary objective of the study was to evaluate the relative importance of the various interactions and

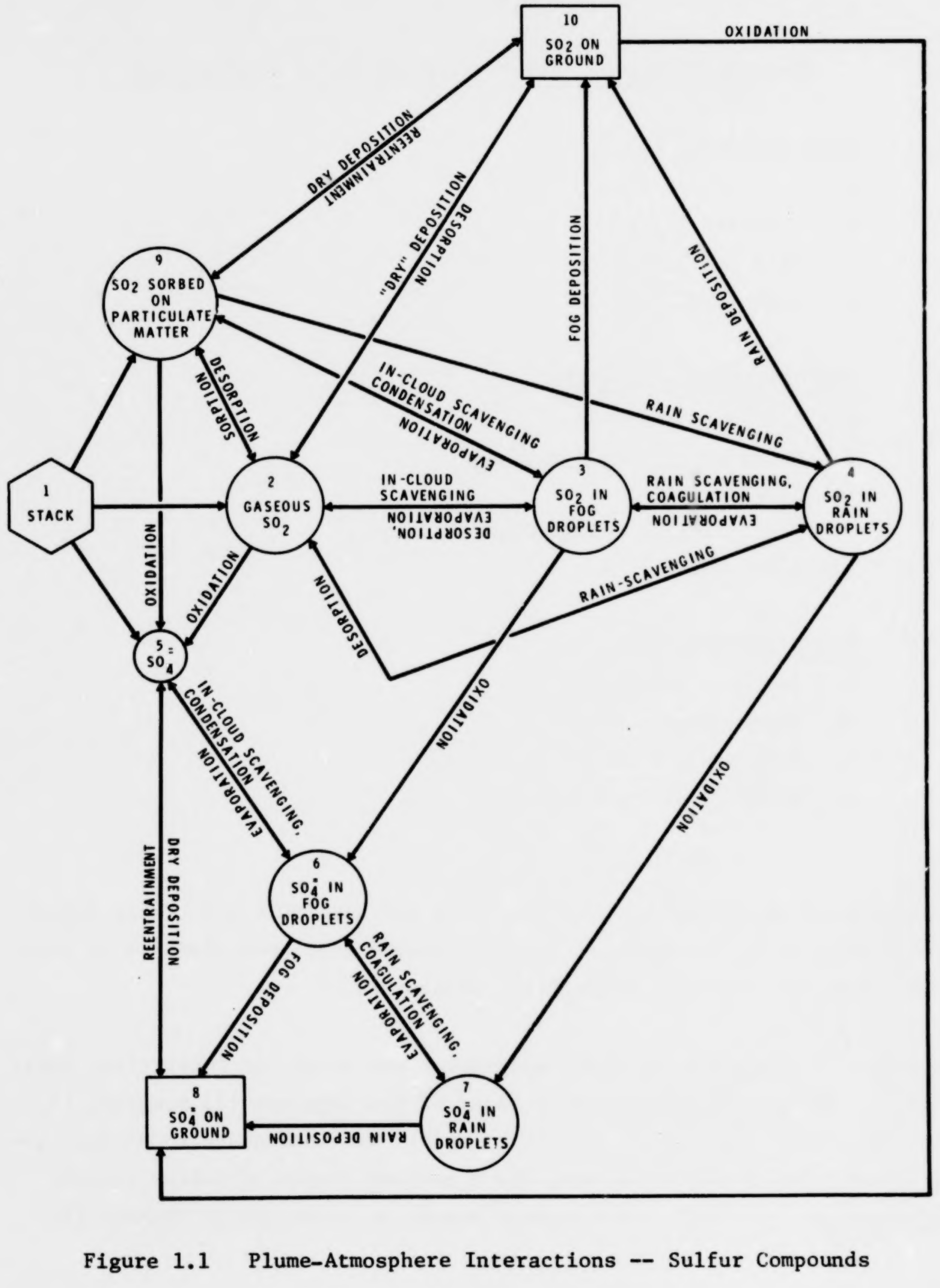
10
SO2 ON GROUND
OXIDATION
DRY DEPOSITION
REENTRAINMENT
"DRY" DEPOSITION
DESORPTION
FOG DEPOSITION
RAIN DEPOSITION
9
SO2 SORBED ON PARTICULATE MATTER
DESORPTION
SORPTION
IN-CLOUD SCAVENGING
CONDENSATION
EVAPORATION
RAIN SCAVENGING
1
STACK
2
GASEOUS SO2
IN-CLOUD SCAVENGING
DESORPTION, EVAPORATION
3
SO2 IN FOG DROPLETS
RAIN SCAVENGING, COAGULATION
EVAPORATION
4
SO2 IN RAIN DROPLETS
OXIDATION
OXIDATION
DESORPTION
RAIN-SCAVENGING
5
SO4=
IN-CLOUD SCAVENGING, CONDENSATION
EVAPORATION
OXIDATION
OXIDATION
REENTRAINMENT
DRY DEPOSITION
6
SO4= IN FOG DROPLETS
FOG DEPOSITION
RAIN SCAVENGING, COAGULATION
EVAPORATION
8
SO4= ON GROUND
7
SO4= IN RAIN DROPLETS
RAIN DEPOSITION

Figure 1.1 Plume–Atmosphere Interactions -- Sulfur Compounds

TABLE 1.1

ATMOSPHERIC FACTORS WHICH INFLUENCE PLUME INTERACTIONS

I. METEOROLOGICAL PARAMETERS
  - A. Temperature Field
  - B. Humidity Field
  - C. Wind and Turbulence Fields
  - D. Solar Radiation

II. PRECIPITATION PARAMETERS
  - A. Precipitation Rate
  - B. Raindrop Size Distribution
  - C. Snow Morphology
  - D. Precipitation Charge Distribution
  - E. Cloud Morphology

III. PLUME PERTURBATIONS
  - A. Buoyancy Effects
  - B. Stack Aerodynamics
  - C. Orographic Effects
  - D. Multi-Plume Interactions

atmospheric variables depicted in Figure 1.1 and Table 1.1. These objectives were to be accomplished by simultaneous field measurements of washout rates and pertinent atmospheric parameters.

Chapter II describes the field experiment and gives the theoretical basis for its design. During an early phase of the experimental program, it became evident that this preliminary theory was inadequate to explain qualitatively the results observed, and a revised theory of sulfur dioxide washout was developed. The revised theory is presented in Chapter III.

A review of the field experiments is presented in Chapter IV. The experimental data are consolidated in Appendix A.

Discussion of the field results in light of the revised theory of Chapter III is presented in Chapter V and study conclusions are contained in the final chapter.

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CHAPTER II

DESCRIPTION OF THE FIELD EXPERIMENT

The experimental approach was based primarily upon the method suggested by May.(2) This technique, which was employed for the measurement of gas and aerosol washout in earlier works,(3,4) involves the collection of precipitation on a surface sampling line which extends across the overhead plume. The mass of material collected by the samplers is compared with the total mass that has passed overhead during the sampling period. The basis for this approach and description of the area, sampling grid, equipment, supporting measurements, and analysis techniques are presented here.

BASIS FOR EXPERIMENTAL CONCEPT

May's technique of analysis is based upon the assumption that washout occurs as a first-order, irreversible process. This method can be visualized most easily by considering a "puff" of plume of mass, m, that has been emitted from the stack and is drifting downwind across the sampling line. By virtue of first-order irreversibility, washout may be equated to the time rate of plume depletion, dm/dt, provided washout is the only mechanism acting to deplete the plume. This process can be represented by

$$\frac{dm}{dt} = - \Lambda m \quad , \qquad (2.1)$$

where the constant Λ is referred to as the washout coefficient.

In terms of the initial mass of the "puff" m_o, the downwind distance x and the mean wind speed $\bar{u}$, Equation 2.1 may be transformed to give

$$\frac{dm}{dx} = -(\Lambda\, m_o/\bar{u})\; e^{-\Lambda x/\bar{u}} \quad . \qquad (2.2)$$

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This relationship provides an experimental means for determining the washout coefficient for a particular pollutant, provided, of course, that the first-order irreversibility assumption is valid. The measurement of dm/dx is accomplished by measuring the total mass of pollutant contained in precipitation, collected in samplers spaced along an arc around the source and extending beyond the edges of the plume. For sampler spacing ΔY,

$$\frac{dm}{dx} = \Sigma m_i \ \Delta Y/A \quad , \tag{2.3}$$

where Σm_i is the total mass recovered from the samplers whose individual collection area is A and m becomes the total mass of plume that has passed overhead during the sample collection period. For short distances and small washout coefficients, the exponential term of Equation 2.2 can be neglected and

$$\Lambda = \Sigma m_i \ \Delta Y \ \bar{u}/(m_o A) \tag{2.4}$$

where m_o is the initial mass of the plume emitted during the sampling period.

An independent calculation of particulate washout can be obtained if the raindrop size spectra are measured and the collection efficiency of the particulate by various raindrop sizes is known. The efficiency is unity if all the particulate lying in the path of the raindrop is removed. This relationship, when the particulate is monodisperse, is given by

$$\Lambda = \pi \ N_T \int_o^\infty a^2 \ E(a) f^*(a) da \tag{2.5}$$

where E(a) denotes collection efficiency and $f^*(a)$ and N_T are the probability-density function and total number of drops falling through a unit area in unit time.

The close agreement of Equations 2.4 and 2.5 has been shown$^{(5)}$ for a case of washout of water soluble particulate by rain. Owing to the solubility of the particulate, it was assumed that it behaved similar to water droplets of equivalent $a^2\rho$, the product of the square of droplet or particle radius and its density. Collection efficiencies for the interaction of water drops and water droplets measured by Kinzer and Cobb$^{(6)}$ were used together with measured rain spectra. The resulting agreement is shown in Figure 2.1.

Although the integrated mass from the precipitation collectors is used for the calculation of the washout coefficient, there is an advantage in analyzing each collector separately. This permits better evaluation of an experiment for it indicates the degree of plume containment, contamination and dry deposition. Figure 2.2 shows the mass of the water-soluble particulate which was recovered from each collector on arcs at 50 ft and 100 ft following the release of 44 grams during a period of 3 minutes in a rainfall of 8.2 mm-hr^{-1}.$^{(7)}$ Plume containment was complete. The near-ideal distributions indicate that contamination was at a minimum. An almost equivalent total mass on both arcs indicated that dry deposition was also minimal.

The washout coefficient for gases also can be determined with this experimental technique providing the initial assumption of a first-order, irreversible process is valid. The calculation of a washout coefficient for gases from raindrop spectra utilizes the equation

$$\Lambda = 4\pi N_o \int_o^\infty a D_{Ay} \text{Sh}(a) f(a)\, da \qquad (2.6)$$

where a is the drop radius, D_{Ay} is the diffusivity of the gas, Sh is the Sherwood number, and f and N_o are the probability-density function and total number of drops existing in a unit volume of space.

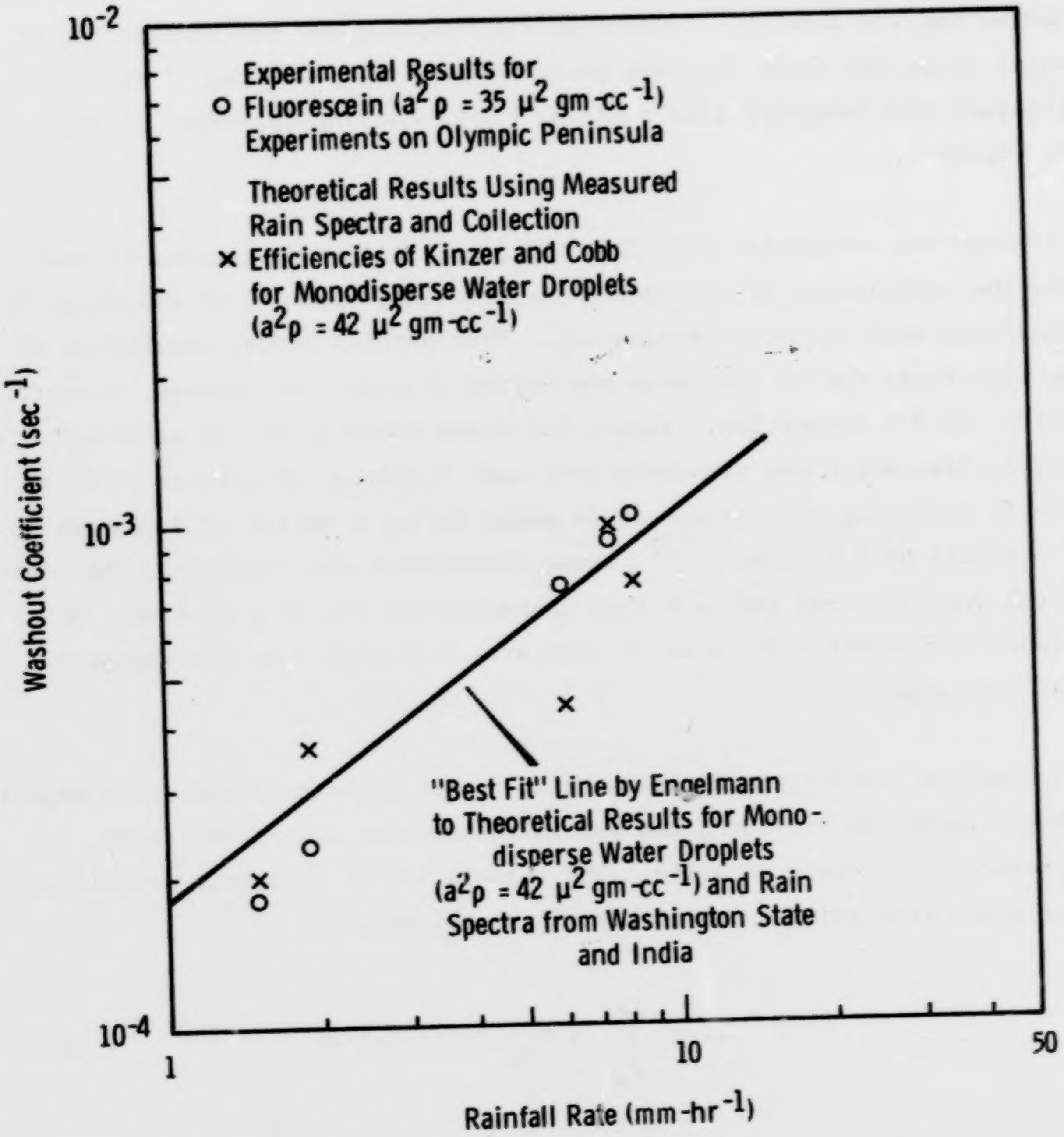


Figure 2.1 Aerosol Washout Coefficients

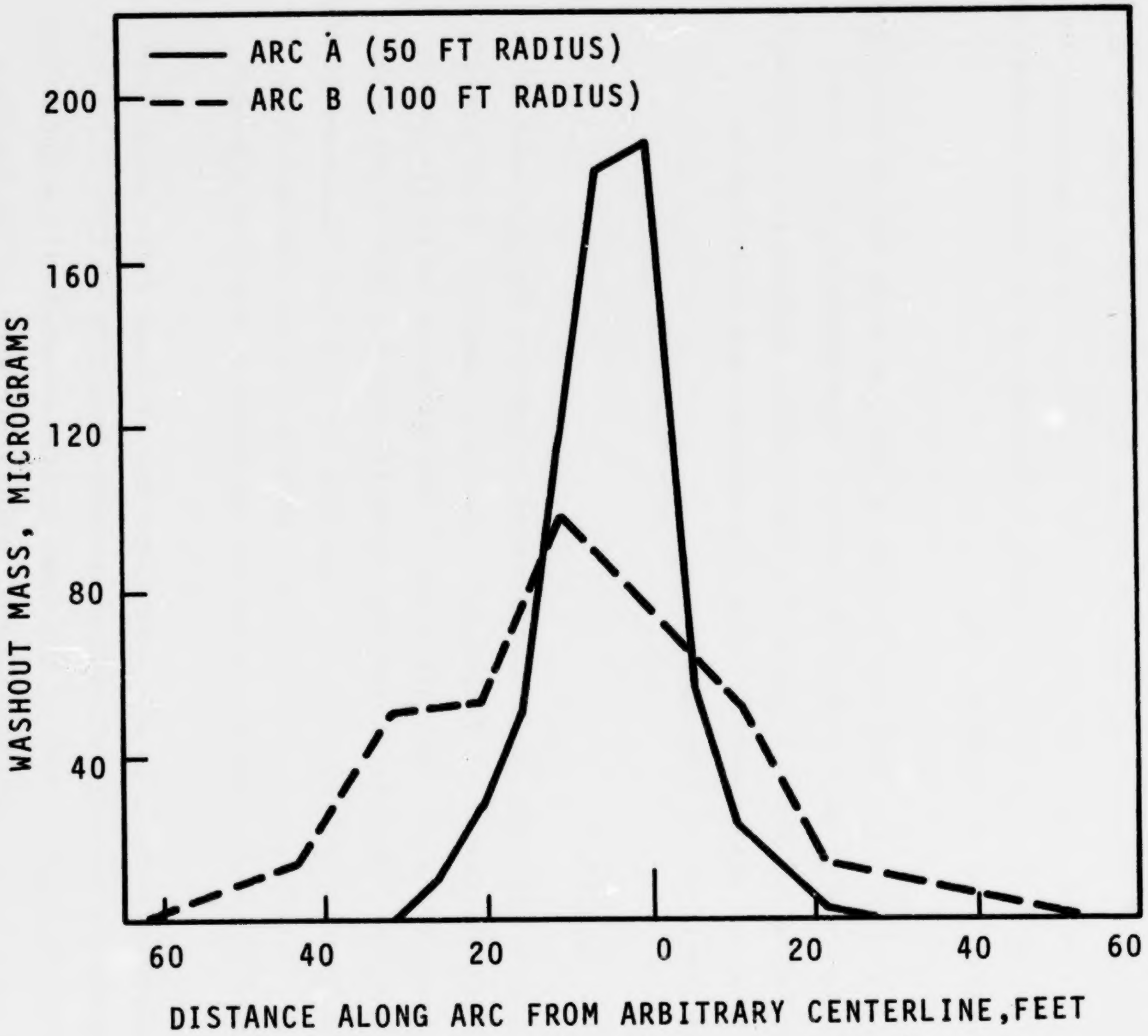


Figure 2.2 Distribution of Fluorescein Aerosol Washout

Comparisons of washout coefficients for gases determined by Equations 2.4 and 2.6 have been less satisfactory, in general, than the previously noted comparisons for particulates. Figure 2.3 is an example of such a comparison. These experiments were conducted to determine the washout coefficient for sulfur dioxide released from a heated gas cylinder mounted on a low tower.(8). Collectors were located on Arcs A and B at distances of 50 ft and 100 ft. Arc A experimental values were about 20 percent of those calculated from the observed raindrop size spectra. Closer agreement was noted on Arc B, but this was attributed to deposition of sulfur dioxide on the collectors from the surface air.

It appeared, therefore, that the initial assumption might not be completely valid in the case of sulfur dioxide washout. Consequently, additional measurements beyond those required for particulate washout were provided for the Keystone experiments. These measurements are described in subsequent sections of this chapter.

DESCRIPTION OF AREA

The Keystone Generating Station is located in western Pennsylvania about 35 miles east-northeast of Pittsburgh. Moderate, westerly winds prevail and extremes of weather are infrequent. Precipitation is fairly evenly distributed over the year, averaging approximately two inches per month. The total annual precipitation for this area is less than elsewhere in the Northeast. During the field experiment periods, it was observed that a large number of storms either passed to the south or north of the area.

Rolling country extends in all directions for at least fifty miles from the Keystone Station with elevations ranging from 1000 to 1500 ft in the vicinity of Keystone. Much of the land is tree covered with a variety of hard and soft woods. Indiana County, immediately east of the Keystone Station is known as the Christmas Tree Capital of the World. There are numerous small farms, in addition to the tree farms, scattered throughout this area of low population. The largest nearby population center is

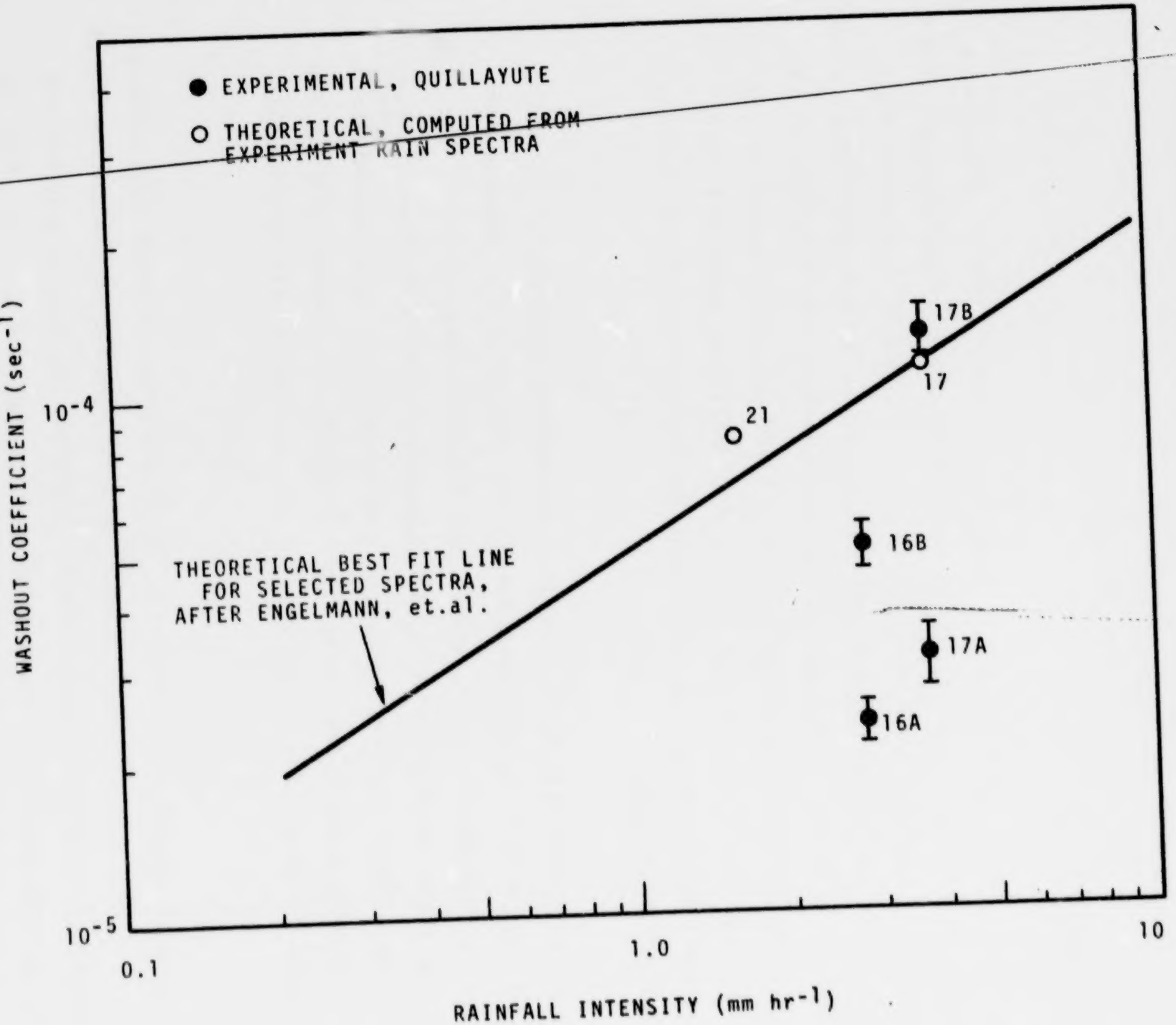


Figure 2.3 Sulfur Dioxide Washout Coefficients

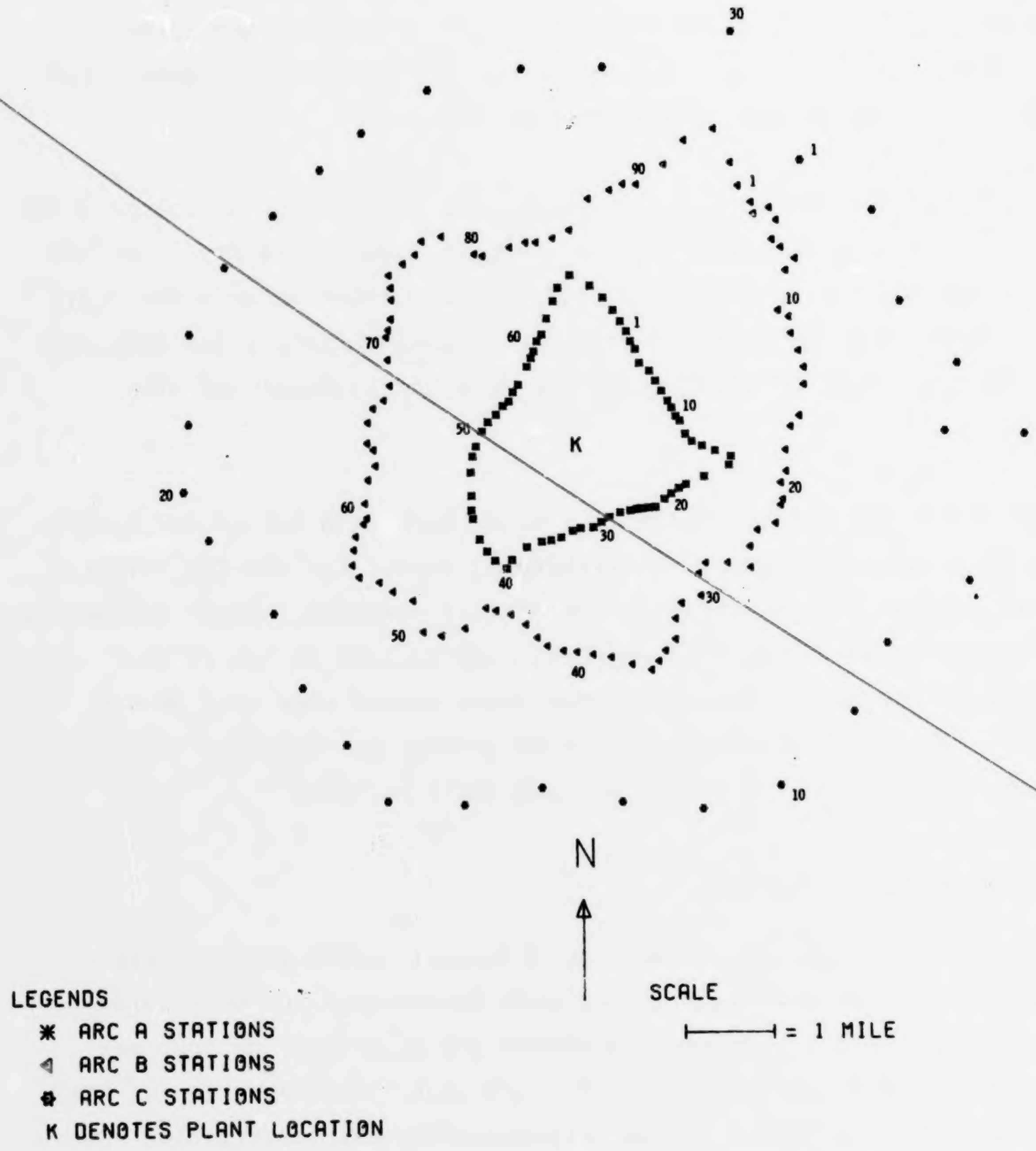
Indiana, which is located about 10 miles to the east. Students at Indiana University of Pennsylvania constitute about half of its population of nearly 25,000.

SAMPLING GRID

The numerous small farms result in a dense network of roads. This was a fortunate circumstance for the field operations which required motor vehicles for rapid deployment of collectors over relatively large distances. Although it is desirable to have the collectors on an arc equidistant from the Keystone Station, a certain amount of compromise was required by the existing road pattern. A collection arc of 90° was anticipated as sufficient coverage for a single experiment, but collector locations were selected to completely enclose the Keystone Station to provide coverage for all wind directions.

These encirclements will be referred to throughout this report as arcs. Arcs A, B, and C were established during the course of the experiments at nominal distances of 1-1/4, 2-1/4, and 4 miles, respectively. The location of these arcs relative to the Keystone Station is shown in Figure 2.4. Also shown are the collector locations which were spaced about 4° apart on Arcs A and B and at nearly 12° on Arc C. Uneven spacing was necessitated by local conditions which might interfere with successful operation.

Collectors were placed at consecutive locations which spanned approximately 90° on Arcs A and B in the experiments, or runs, conducted during the first field period in October-November, 1969. Apparent failure to contain the plume during that period resulted in extending the arcs to about 180° by sampling every other location. To extend the arc by doubling the number of collectors would have resulted in increasing the deployment and retrieval times, thereby reducing the period for concurrent sampling by all collectors. The increased spacing was particularly necessary on Arc C to provide coverage at that distance.


30
1
90
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80
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N
LEGENDS
✱ ARC A STATIONS
◄ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALE
= 1 MILE

Figure 2.4 Sampling Grid

PRECIPITATION COLLECTORS

Different collectors were used for rainfall and snowfall. In the case of rainfall, polyvinyl chloride funnels were fitted to waste cans of approximately 1000 sq cm collection area. A polyethylene bottle containing 5 cc of tetrachloromercurate (TCM) solution was attached to a perforated cap on the stem of each funnel. The bottle was removed from the funnel and capped for transit to the laboratory upon retrieval.

The funnel was replaced by a polyethylene bag for the collection of snow. The bag fitted into the waste can and snuggly covered its rim. The TCM solution was omitted on the basis that the low temperatures would inhibit sulfur dioxide loss or chemical reaction. Upon retrieval, the snow was shaken into a corner of the bag and the open end gathered and tied securely.

In addition to the primary collectors which were used for sulfur dioxide and sulfate analysis, identical collectors, except for the TCM solution, provided samples for pH, nitrate, and nitrite analyses. These collectors were located at the background sampling location and at two to four locations on the arcs during the first field period when only pH was measured. The secondary collectors were located at alternate primary sampling locations during the second and third periods.

ADDITIONAL GRID MEASUREMENTS

Emphasis was placed on the collection of precipitation samples, but additional measurements were made on the grid during each run to provide support data. At the background location and at as many as four arc locations, portable generators provided power for the operation of high volume air samplers, bubblers, and precipitation characterization instrumentation.

The high volume samplers were provided to collect airborne sulfate on filter paper for determination of its concentration in air. These were located in standard NASN (National Air Sampling Network) shelters. Use of the high-volume samplers was suspended after early experiments as it became apparent that the sample sizes obtained were too small for reliable analysis. The bubblers which were operated to determine sulfur dioxide concentrations in air sampled at a rate of approximately 0.5 liters per minute, controlled by hypodermic needle orifices. Raindrop size and electric charge spectrometers were operated on the sampling arcs and at upwind locations to establish background values. The importance of drop size spectra is shown in Equations 2.5 and 2.6. Charge may be important if the sulfur is present as particulate. During the February period, snowflake character was recorded photographically.

WIND VELOCITY PROFILE

The introduction of heated pollutant into the atmosphere at a height of 800 ft necessitates the definitions of wind velocity to well above that height. This was accomplished using single-theodolite pibals released from the Overlook — a visitor center located about 200 ft above the base of the Keystone Generating Plant on a hill about one-half mile to the southeast. This location provided an unobstructed view of the sounding balloon. The 30 gram balloon was inflated to one-half standard free-lift to reduce the ascension rate, and position readings were taken at 30 sec intervals. A release was made prior to each run to estimate the plume centerline for arc deployment and, insofar as practical, hourly releases were made during the run for continued operational guidance and documentation.

An average ascension rate was determined with double-theodolite soundings during fair weather and this rate was assumed for subsequent single-theodolite soundings. Except during periods of heavy rainfall, little deviation from the predetermined ascension rate was noted. A problem which did arise, particularly during the February series, was that low ceilings and condensation from the Keystone Station prevented tracking to the desired elevation.

AERIAL AND MOBILE GROUND-LEVEL SAMPLING

Aerial sampling was conducted using a Cessna 172 aircraft equipped to measure and record sulfur dioxide concentration, temperature, airspeed, humidity, altitude, and time. These variables were recorded on magnetic tape using a DL620A recorder manufactured by Metrodata Systems, Incorporated of Norman, Oklahoma. Temperature, airspeed, humidity, and altitude measurements were made using a TVH26 instrument package, also manufactured by Metrodata. Sulfur dioxide was measured using an analyzer and scrubber, manufactured by Sign-X, Inc. of Essex, Connecticut. Laboratory calibrations of the sulfur dioxide analyzer are given in Appendix C.

The sampling probe for sulfur dioxide measurement was located on the leading edge of the right wing, approximately four feet from the fuselage. The probe passed into the wing interior and then into the cockpit to the analyzer. Humidity and temperature sensors were mounted on the right wing strut. The pitot-tube airspeed sensor was mounted on the left wing next to the aircraft pitot-tube.

Plume sampling was conducted by flying normal to the plume "centerline" between two appropriate landmarks at a constant airspeed of 80 mph. Traverses were flown at vertical intervals of 100 and 200 ft. During the Spring phase of the study, it became increasingly evident that sulfur dioxide concentrations near the ground were more critical in influencing washout than were those aloft. For this reason, the sulfur dioxide analyzer was adapted for mobile ground-level sampling and placed in a vehicle. Sampling was accomplished by driving along the sampling arcs and recording sulfur dioxide levels at each station.

Ground level sulfur dioxide concentrations on Arcs A and B were generally too low to detect plume location with the Sign-X analyzer; on Arc C, however, the plume could usually be detected, although peak sulfur dioxide levels were generally only a few hundredths of a part per million.

All of the aircraft sampling equipment performed satisfactorily, but aircraft operation was limited by low ceilings and low visibility during rainfall and snowfall. Integral components of the aircraft instrumentation were detained enroute to Pennsylvania for the third period investigation by a Teamster wildcat strike. This instrumentation, as well as other equipment, was not released during April and the aircraft was not employed during that sampling period.

Airborne particulate matter was sampled on occasion using a Unico cascade impactor. Particle morphology and size distributions were similar to those observed in the comprehensive study reported by MRI.(9)

LABORATORY ANALYSES

With the exception of some pH measurements all chemical analyses of the study were performed in a mobile field laboratory, located adjacent to the APCO field office at Jimmy Stewart Airport in Indiana County. All of the collected samples were analyzed for sulfur dioxide content. Selected samples were analyzed for sulfate ($SO_4^=$), nitrate (NO_3^-), nitrite (NO_2^-), and pH.

Upon their collection, the samples were delivered to the mobile laboratory for analysis, as quickly as possible, to minimize deterioration. If it became necessary to postpone their analysis for more than a few hours the samples were refrigerated.

SULFUR DIOXIDE ANALYSIS -- Sulfur dioxide was analyzed using the sulfamic acid variation of the West and Gaeke method.(10) A 2.5 ml aliquot of each sample was withdrawn using an individual hypodermic syringe and transferred into a sampling cup of the Technicon Autoanalyzer for subsequent automated analysis. This technique allowed measurement of samples as small as 0.1 micromole sulfur dioxide per liter of water. Tests showed the results to be reproducible to within about 2 percent. Overall error of the method was expected to be less than about 5 percent.

Aliquots from several samples were withdrawn and analyzed at various time intervals to check for deterioration. These tests showed that no significant loss of sulfur dioxide occurred for several hours after sample collection.

Analysis of snow samples was conducted in a somewhat different manner owing to the absence of TCM solution during the collection period. Here the plastic bags which contained the samples were suspended in the laboratory, and 2.5 ml of TCM solution was injected into each. The snow was allowed to melt and the bags were shaken to mix their contents. Upon complete melting 2.5 ml aliquots were withdrawn from each bag and analyzed for sulfur dioxide, using the techniques described above for rain samples.

SULFATE ANALYSIS -- Sulfate content of the samples was analyzed using the turbidimetric barium chloride method.(11) This technique was chosen over the more elegant barium chloroanilate(12) and titration(13) methods because it was found to be the least affected by the presence of TCM solution.* A Bausch and Lomb Spectronic 20 photometer was employed for the majority of these analyses.

Sulfate results exhibited a large amount of scatter — behavior typical of turbidimetric data. The majority of this scatter, however, was suspected to have arisen from artifacts within the samples. Scatter from purely analytical factors is expected to be about 15 percent.(11)

NITRATE ANALYSIS -- Nitrate levels of selected samples were measured using the chromotropic acid method of West and Ramachandran.(14,15) This technique was time-consuming and tedious, but was felt to give quite reliable results. Much of the scatter that occurred in the results was suspected to have occurred from artifacts within the samples.

Nitrate measurements were made only with samples that did not contain TCM solution, and every effort was made to insure that these analyses were performed as soon as possible after sample collection.

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*The presence of TCM solution was felt to be important here because it tended to prevent further sulfate production within the sample during the time period between collection and analysis.

NITRITE ANALYSIS -- Nitrite was analyzed using a variation of the well-known Saltzmann method. Few successful nitrite analyses were completed, owing to its rapid decomposition. A certain degree of success was achieved finally by adding the Saltzmann reagent to the rain sample in the field immediately upon collection; however, it appears that significant decomposition may have occurred even under these circumstances.

Measurement of the pH of selected samples was accomplished using a pH meter. Most of these measurements were taken in the field so as to minimize the time between sampling and analysis. During the fall 1969 series, pH measurements were taken before and after sparging of the samples with nitrogen. This gave inconclusive results and was discontinued for the duration of the study.

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CHAPTER III

THEORETICAL ASPECTS OF GAS WASHOUT BY RAIN

The profusion of theoretical publications in the meteorological literature concerning precipitation washout of atmospheric particulates contrasts sharply with the relative dearth of such material related to gas washout phenomena. Interpretation of the data obtained in this investigation depends strongly upon the development of an adequate theoretical basis for the analysis of below-cloud, gas washout processes. It can be demonstrated rather conclusively (cf. Appendix B) that sulfur dioxide washout by rain-capture of sulfur dioxide-containing fog droplets is insignificant compared to gas washout through simple gas absorption by rain (cf. steps 2-3-4-10 and 2-4-10 in Figure 1.1). For this reason Chapter III will deal only with the simple gas washout process.

The first section deals with the individual rate processes contributing to the overall gas washout phenomenon. These are related to the net rate of washout, and methods for estimating their magnitudes are described. Subsequently, these methods are employed to define limiting situations in an attempt to bracket behavior exhibited by real systems. The section concludes with a discussion of some of the laboratory methods used previously to measure gas washout, indicating their various advantages, limitations, and applicability to the present study.

The second section of this chapter deals exclusively with thermodynamic aspects, i.e., chemical reaction and solubility equilibria as they relate to washout behavior.

The material presented here pertains specifically to the washout of sulfur dioxide; however, its applicability is rather general and it can be used as a preliminary basis for theoretical analysis of all systems in which gas washout occurs.

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RATE PHENOMENA

DEFINITION OF MASS-TRANSFER COEFFICIENTS -- It is customary to visualize the phenomenon of gas absorption by a falling drop to occur as a consecutive, two-step process. The gas migrates first from the bulk medium to the drop surface, whereupon it mixes into the interior of the liquid. Such a visualization will be shown later to be highly superficial; it does, however, suffice to provide a mathematical framework which can be "forced" to fit physical behavior upon subsequent manipulation of the pertinent parameters.

For trace-gas washout, this two-step process can be represented mathematically by the equations*

gas-phase step:

$$N_{Ao} = - k_y (y_{Ab} - y_{Ao}) \tag{3.1}$$

liquid-phase step:

$$N_{Ao} = - k_x (x_{Ao} - x_{Ab}) \quad . \tag{3.2}$$

Here N_{Ao} is the average molar flux of material A† passing through the liquid -vapor interface, and x_A and y_A denote mole fractions of A in the liquid and gas phases, respectively. The subscripts b and o pertain to bulk (average) and interfacial conditions. k_y and k_x are known as the gas-phase and liquid-phase mass-transfer coefficients, respectively. The convention will be used that fluxes passing from the drop are positive entities.

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*The development here is based partially upon that given by Bird, et al.(16). Nomenclature used here is consistent with that employed by these authors.

†A flux is defined here as the rate of the passage of material through a cross section of unit area.

Equations 3.1 and 3.2 find their theoretical basis in the simplified film-theory visualization as characterized in Figure 3.1. Here the two consecutive steps occur across the thin liquid and gaseous films bordering the drop interface. From Fick's law of diffusion(17)

$$N_{Ao} = - c_y D_{Ey} \frac{dy_A}{dr} = - c_x D_{Ex} \frac{dx_A}{dr} \quad , \qquad (3.3)$$

which may be written

$$N_{Ao} = - \frac{c_y D_{Ey}}{\delta_y} (y_{Ab} - y_{Ao}) = - \frac{c_x D_{Ex}}{\delta_x} (x_{Ao} - x_{Ab}) \quad , \qquad (3.4)$$

which reduces to Equations 3.1 and 3.2 upon making the obvious substitutions of the mass-transfer coefficients. Here D_{Ey} and D_{Ex} denote effective diffusivities in the gas and liquid phases, and δ_x and δ_y are the liquid and gas "film thicknesses." c denotes total molar concentration. None of the entities comprising k_x and k_y should be expected to vary appreciably with the mole fraction of A, hence this simplified film theory implies that the mass-transfer coefficients should not vary with the concentration of the gas being washed out. Such behavior may or may not be observed in the complex physical situations that occur in nature; the reasons for this will be discussed in a later section.

Usually Equations 3.1 and 3.2 are not employed directly to determine mass-transport rates because of the difficulty in determining the interfacial concentrations x_{Ao} and y_{Ao}. This problem is overcome by defining a new coefficient K_y based upon the overall concentration driving-force between the bulk gas and the bulk of the liquid;

$$N_{Ao} = - K_y (y_{Ab} - y_{Ae}) \quad . \qquad (3.5)$$

Here y_{Ae} is the mole fraction of component A that would exist in the gas phase in equilibrium with the bulk liquid of mole fraction x_{Ab}. K_y is

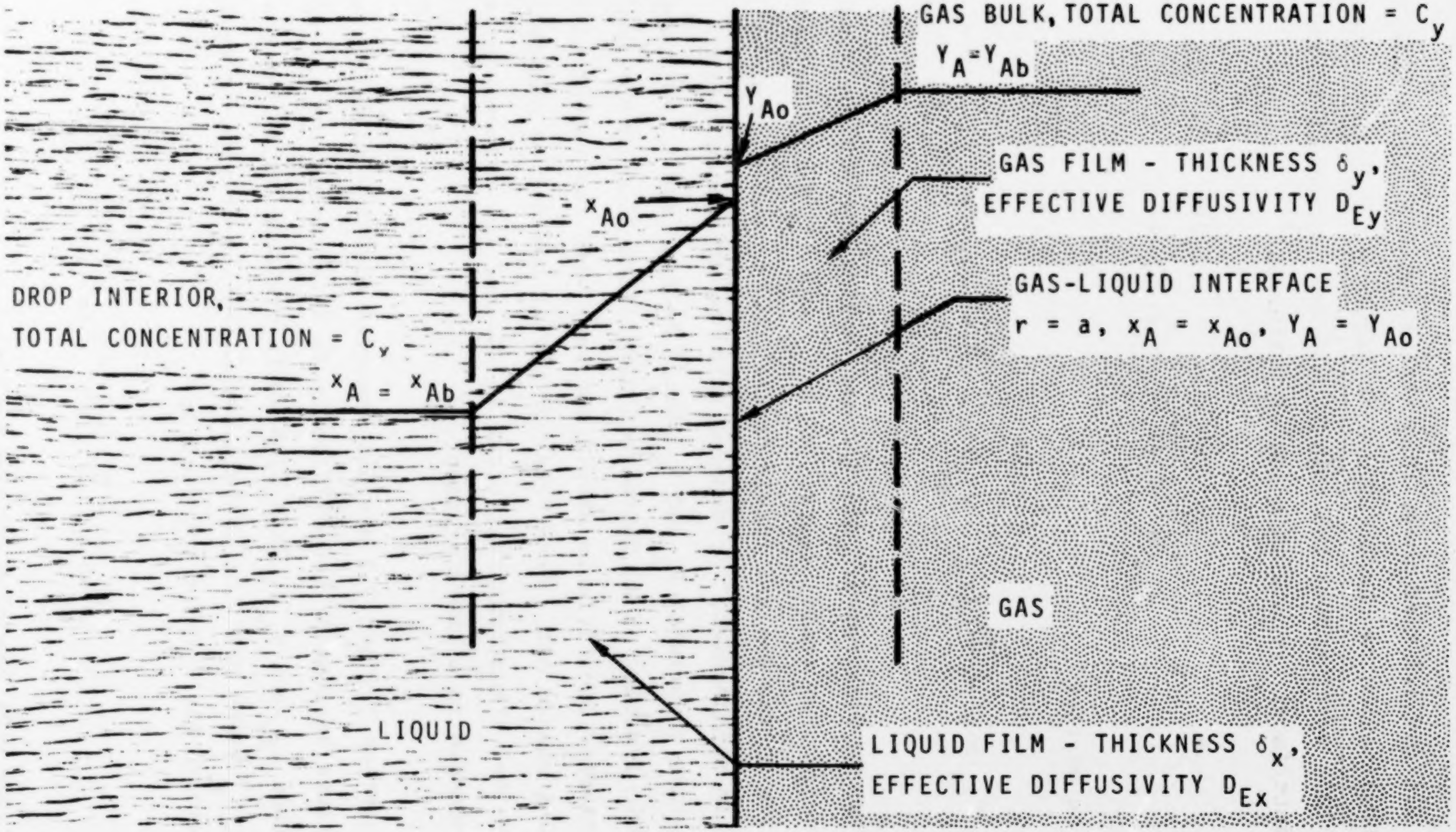
GAS BULK, TOTAL CONCENTRATION = C_y
$y_A = y_{Ab}$
y_{Ao}
GAS FILM - THICKNESS δ_y, EFFECTIVE DIFFUSIVITY D_{Ey}
x_{Ao}
GAS-LIQUID INTERFACE
$r = a$, $x_A = x_{Ao}$, $y_A = y_{Ao}$
DROP INTERIOR, TOTAL CONCENTRATION = C_y
$x_A = x_{Ab}$
GAS
LIQUID
LIQUID FILM - THICKNESS δ_x, EFFECTIVE DIFFUSIVITY D_{Ex}

Figure 3.1 Representation of Simplified Film Theory

known as the overall mass-transfer coefficient based on the gas-phase driving force. y_{Ae} is determined from x_{Ab} using equilibrium data, which may be expressed in functional form as

$$y_A = g(x_A) \quad . \tag{3.6}$$

In the special case where this relationship is linear, Equation 3.6 reduces to

$$y_A = Hx_A \quad . \tag{3.7}$$

Systems conforming to Equation 3.7 are said to obey Henry's law;(18) H is known as the Henry's-law constant. It should be emphasized here that solutions of sulfur dioxide in water do not obey Henry's law; equilibrium behavior of such solutions is examined in more detail in the second section of this chapter.

RELATIONSHIP BETWEEN THE MASS-TRANSFER COEFFICIENTS -- The equilibrium relationship, Equation 3.6, can be employed to express the overall mass-transfer coefficient in terms of k_x and k_y by combining Equation 3.1, 3.2, and 3.5. The outcome is given by

$$\frac{1}{K_y} = \frac{m_y}{k_x} + \frac{1}{k_y} \quad , \tag{3.8}$$

m_y denoting the slope of the equilibrium curve "somewhere" between x_{Ab} and x_{Ao}; and

$$m_y = \frac{y_{Ae} - y_{Ao}}{x_{Ab} - x_{Ao}} \quad . \tag{3.9}$$

For systems obeying Henry's law m_y is simply the constant, H.

Various types of washout behavior can be identified on the basis of Equation 3.5. If K_y is truly a constant independent of y_{Ab} and y_{Ae}, the process is said to be first order. If, further, A is annihilated completely upon contacting the drop surface (total retention), $y_{Ae} = 0$ and the washout process is first order, irreversible. Often, when K_y is not constant, the process can be "linearized" by choosing some intermediate value of the mass-transfer coefficient, α, such that

$$N_{Ao} = - \alpha \left(y_{Ab} - y_{Ae}\right) \quad \text{, approximately.} \qquad (3.10)$$

Equation 3.10 is said to express the phenomenon as a psuedo first-order process.

RELATIONSHIPS BETWEEN MASS-TRANSFER COEFFICIENTS, WASHOUT RATES, AND WASHOUT COEFFICIENTS -- The ultimate objective of determining values of the mass-transfer coefficients is their utilization to compute net washout behavior. The net washout rate, w, defined as the rate of removal from the air of material A by precipitation within a unit volume element, v, can be expressed in terms of the mass-transfer coefficient by summing the mass-transfer rates for all of the drops in v. Thus, if the precipitation is composed of spherical, noninteracting drops*

$$w = - 4\pi N_o \int_o^\infty a^2 \, f(a) \, N_{Ao}(a) \, da$$

$$= 4\pi N_o \int_o^\infty a^2 \, f(a) K_y(a) (y_{Ab} - y_{Ae}) \, da \quad , \qquad (3.11)$$

---

*The assumption of spherical drops has been shown elsewhere$^{(19)}$ to be sufficiently valid for the purposes of this investigation. Noninteraction is considered to be a reasonably valid assumption for most rain situations insofar as gas washout is concerned owing to the high rates of diffusive transport relative to the occurrence rate for drop interactions (i.e., collisions, competition for material, wake interactions, etc.).

where a denotes drop radius, N_o is the total number of drops in v, and f(a) is the probability density function for raindrops in v.

As noted in Chapter II, most previous analyses of atmospheric washout processes have employed the assumption of total retention by the drop and have expressed the washout rate in terms of an overall washout coefficient, Λ_i;

$$w = \Lambda_i \, y_{Ab} \, c_y \quad , \tag{3.12}$$

(first-order, irreversible process).

Here the subscript i has been added to emphasize that the assumption of irreversibility has been employed. Λ_i can be expressed in terms of the individual washout coefficients for drops of different sizes λ_i as follows, provided that the drops do not interact.

$$\Lambda_i = N_o \int_o^\infty f(a) \, \lambda_i(a) \, da \quad . \tag{3.13}$$

From Equations 3.11, 3.12, and 3.13, the following expressions can be obtained relating the washout coefficient to the overall mass-transfer coefficient, K_y.

$$\Lambda_i = \frac{4\pi N_o}{c_y} \int_o^\infty a^2 \, K_y \, f(a) \, da \tag{3.14}$$

(first-order irreversible process) ,

$$\lambda_i(a) = \frac{4\pi a^2}{c_y} K_y$$

(first-order irreversible process) . (3.15)

For the washout of gases, irreversibility is generally a poor assumption and the use of Λ_i should be discouraged. This can be overcome by redefining the washout coefficient in terms of a reversible process, thus

$$w = \Lambda_r \, (y_{Ab} - y_{Ae}) \, c_y \qquad , \qquad (3.16)$$

illustrating that reversible washout can be treated equally well in terms of mass-transfer coefficients or in terms of a properly-defined washout coefficient. Because of the danger of confusing reversible and irreversible washout coefficients, the theoretical development is continued mainly in terms of the mass-transfer coefficient. This is in concordance with the related field of chemical engineering, where most of the pertinent work regarding gas washout by falling drops has been performed up to the present time.

The net amount of material A carried to the ground by washout can be related to K_y, provided again that the assumptions of sphericity and noninteraction are valid. For this purpose, it is convenient to visualize precipitation being collected in a bucket located somewhere beneath the plume as shown in Figure 3.2. Drops of different sizes entering the collector will have passed through the plume in different trajectories depending upon their terminal velocities and interactions with the wind. These trajectories may be defined by the family of space curves $C_a(x,y,z)$. Also, the drop velocity $\bar{v}_a(x,y,z)$ is defined as $d\bar{r}_a/dt$ where $\bar{r}_a$ denotes a position vector originating at the collector and tracing out the space curve C_a.

For the present, it is assumed that wind parameters and plume concentrations are fixed in time*. The total amount of A picked up by a drop of radius a

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*Time fluctuations in wind parameters and plume concentrations will give rise to time-averaged values of y_A. Such averaged values can be employed in this analysis in lieu of "instantaneous" measurements; however, such a treatment is totally valid for first-order systems only. A discussion of this problem is given in Appendix B.

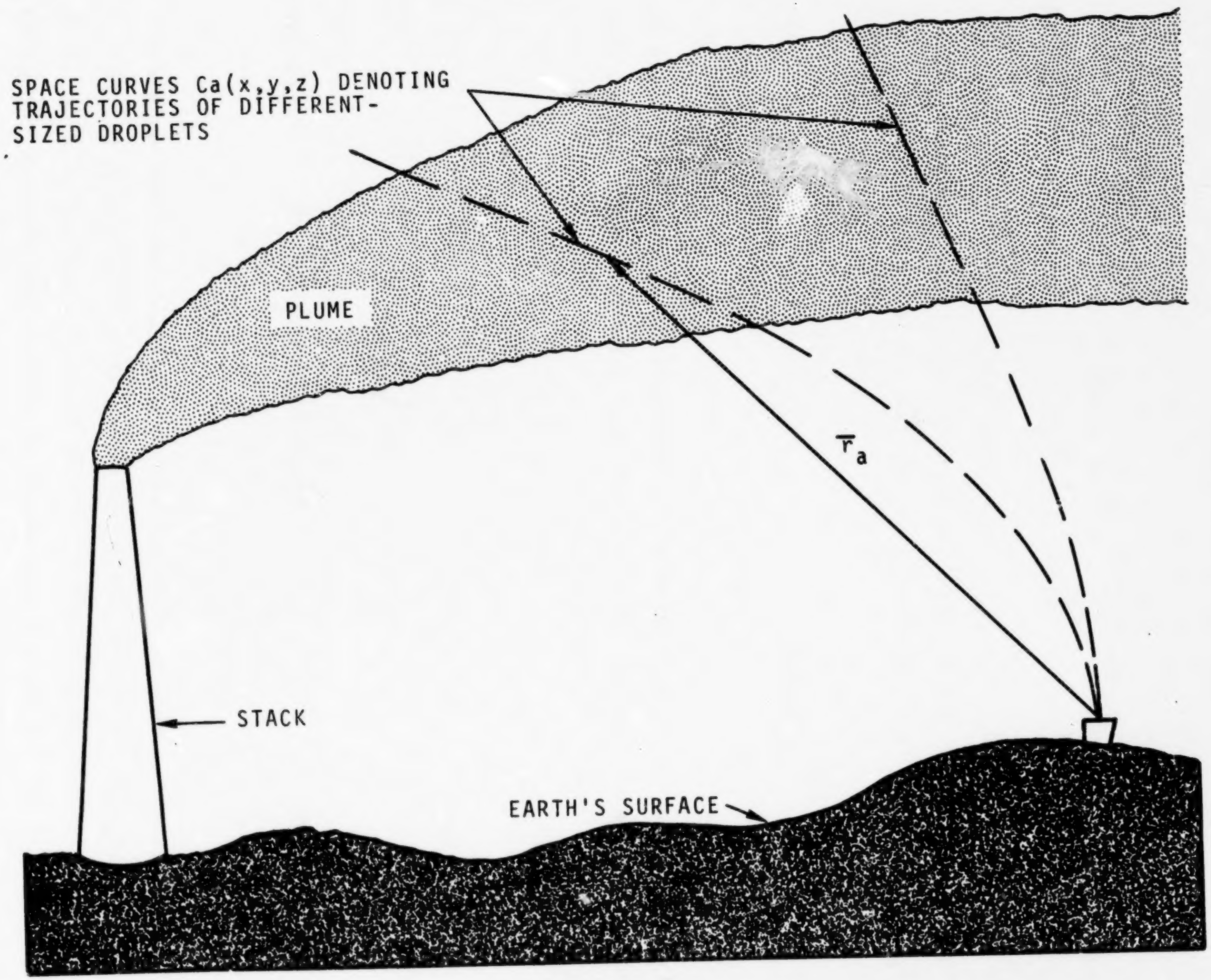
SPACE CURVES Ca(x,y,z) DENOTING TRAJECTORIES OF DIFFERENT-SIZED DROPLETS
PLUME
$\overline{r}_a$
STACK
EARTH'S SURFACE

Figure 3.2   Trajectories of Various Sizes of Raindrops

during its time of passage, t_o, then is given by

$$\xi_a = 4\pi a^2 \int_o^{t_o} K_y \; (y_{Ab} - y_{Ae}) \; dt \quad . \tag{3.17}$$

Since y_{Ab} and y_{Ae} (and, perhaps, K_y as well) vary with x, y, and z, it is convenient to express the integral in terms of position. Since $d\bar{r}_a/dt = \bar{v}_a$, ξ_a is related to a line integral along the curve C_a as follows:

$$\xi_a = 4\pi a^2 \int_{C_a} K_y \; (y_{Ab} - y_{Ae}) \frac{1}{\bar{\bar{v}}_a} \cdot d\bar{r}_a \quad . \tag{3.18}$$

Finally, this may be integrated over the spectrum of drop sizes to give Z, the total amount of A being collected per unit time in a collector of unit cross-sectional area

$$Z = N_T \int_o^{\infty} \xi_a \; f^*(a) \; da + Z_o$$

$$= 4\pi N_T \int_o^{\infty} a^2 f^*(a) \int_{C_a} \frac{K_y (y_{Ab} - y_{Ae})}{\bar{\bar{v}}_a} \cdot d\bar{r}_a \; da + Z_o \quad . \tag{3.19}$$

Here, N_T is the total number of drops that are falling into the unit collector per unit time, $f^*(a)$ is the probability density function for the spectrum of collected drops*, and Z_o equals the total amount of A captured per unit time by the collected rain prior to its passage through the plume, i.e., the background.

---

*Here one should note the difference between $f^*(a)$ and the probability density for raindrops existing in a volume element of atmosphere (denoted by $f(a)$). Generally $f^*(a) = -N_o/N_T \; f(a) \; v_t$, where v_t denotes the terminal fall velocity, dz/dt.

It is emphasized here that Z is an instantaneous entity, and the total amount of A collected over a given sampling period must be expressed in terms of an additional integral in time. If wind and plume parameters fluctuate appreciably during the sampling period, one must again contend with the problem of averaging as discussed in Appendix B.

Equation 3.19 is an important result. It indicates how K_y is used to calculate washout to the earth's surface, and it shows some of the requirements for determining K_y experimentally in the field. If K_y were known, one could employ Equation 3.19 to calculate Z on the basis of rain, wind, plume concentration, and solubility data. Generally the converse is not true. That is, by measuring Z in the field, one cannot determine K_y on the basis of Equation 3.19 alone, unless some additional information regarding the nature of K_y is known. This is a problem that arises consistently whenever the interpretation of differential quantities on the basis of integral data is attempted. Equation 3.19 indicates, however, that data pertaining to N_T, $f^*(a)$, y_{Ab}, $\bar{v}_a$, Z, Z_o, and solubility are necessary (but probably not sufficient) for determining K_y from field measurements.

ESTIMATION OF INDIVIDUAL COEFFICIENTS -- Equations 3.11 and 3.19 indicate how the overall mass-transfer coefficient, K_y, may be employed to determine the washout rates w and Z. K_y, in turn, depends upon the individual coefficients k_x and k_y as indicated by Equation 3.8. From this, it is apparent that the degree of success in analyzing gas washout behavior should depend largely upon an ability to estimate these coefficients. The present section is addressed to this task.

Gas-Phase Mass-Transfer Coefficients -- The transport of gas to the surface of a falling drop occurs primarily by diffusion and convection. This relative simplicity contrasts sharply with complexities exhibited during the process of aerosol washout where the additional effects of inertia, electrical charging, diffusiophoresis, and thermophoresis may become important.(20,21) For the case of purely convective-diffusive transport the gas-phase mass-transfer coefficients can be calculated from the generalized semiempirical expression(16)

$$Sh = 2 + 0.6\ Re^{1/2}\ Sc^{1/3} \quad , \tag{3.20}$$

where

$$Sh = \frac{2k_y\ a}{D_{Ay}\ c_y} \quad = \text{ Sherwood number,}$$

$$Re = \left|\frac{2a\ v_t}{\nu}\right| \quad = \text{ Reynolds number,}$$

and

$$Sc = \frac{\nu}{D_{Ay}} \quad = \text{ Schmidt number.}$$

Here c_y denotes total gas concentration, D_{Ay} is the diffusion coefficient in the gas, v_t is the terminal velocity of the drop, and ν is the kinematic viscosity of air. Equation 3.20 often is referred to as the Frössling(22) equation. It has been shown to describe physical behavior with reasonable accuracy over all conditions of practical interest to the present investigation.(23)

Since the terminal fall velocity v_t can be expressed as a function of drop size (cf. Figure 3.3), the Sherwood number and, therefore, k_y can be represented in terms of drop size and the appropriate gas properties. Such a representation is provided in Figure 3.4, which is essentially a plot of Equation 3.20, based upon the physical properties of sulfur dioxide and air at 20°C, shown in Table 3.1.

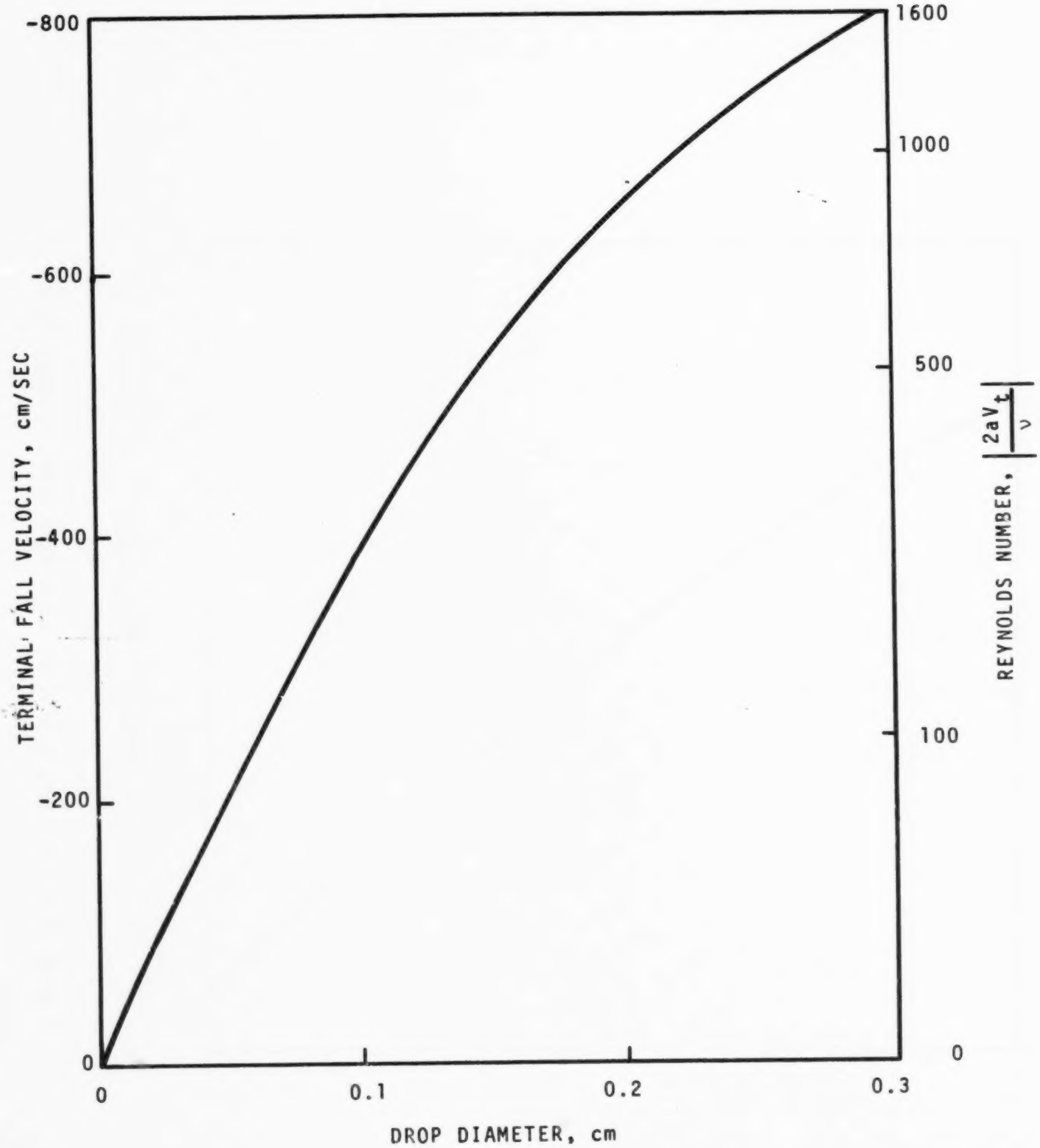

Figure 3.3 Terminal Fall Velocity of Raindrops as a Function of Diameter - Data of Gunn and Kinzer(19)

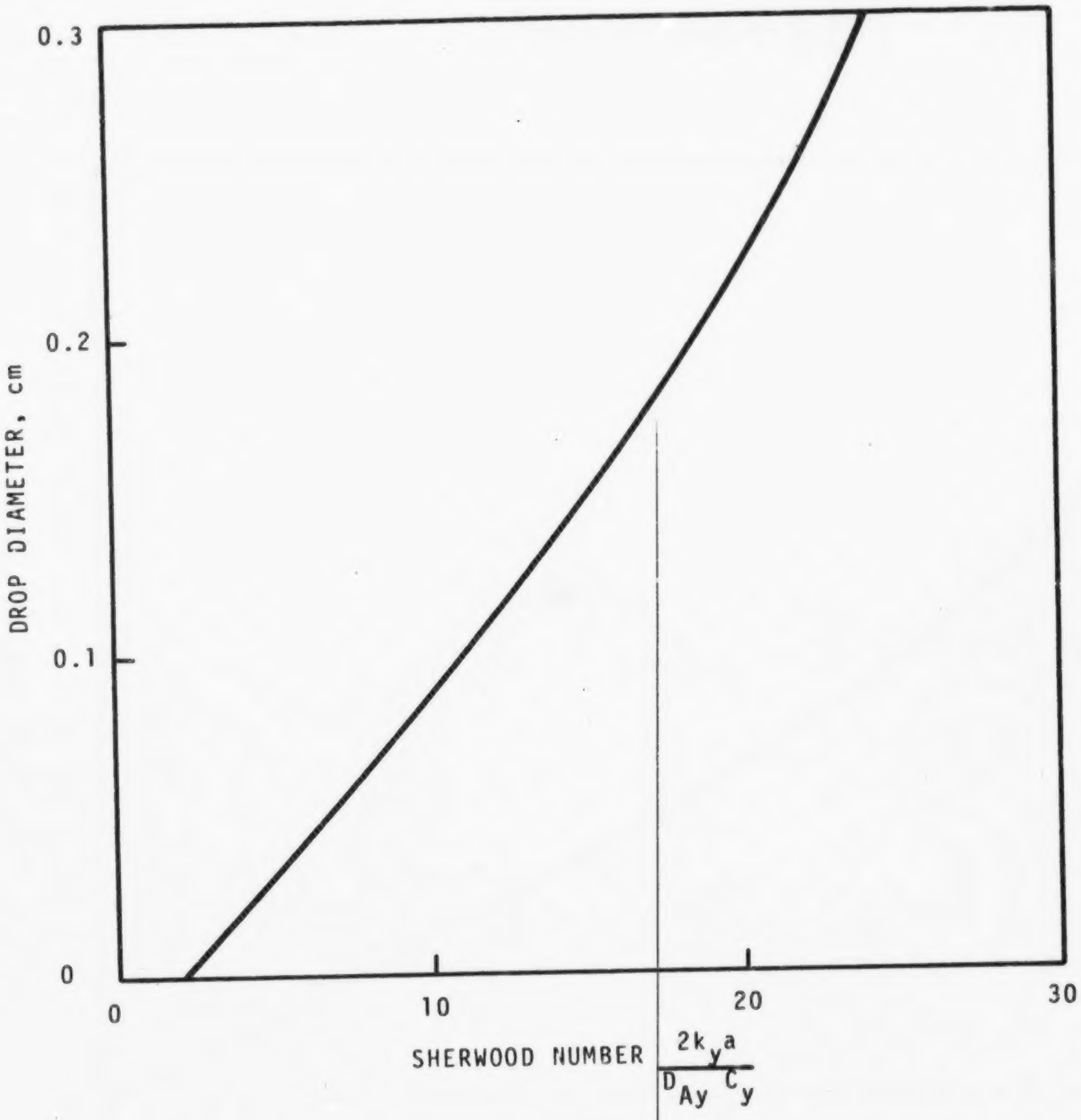

Figure 3.4 Sherwood Number as a Function of Drop Size

TABLE 3.1

SULFUR DIOXIDE - AIR PROPERTIES USED IN CALCULATING k_y

Diffusion Coefficient cm^2/sec	Kinematic Viscosity cm^2/sec	Gas Concentration $moles/cm^3$
0.195	0.1505	4.152×10^{-5}

Liquid-Phase Mass-Transfer Coefficient - General Comments -- The ease with which gas-phase coefficients can be estimated is not matched by similar behavior exhibited within drops. The already complex processes of liquid mixing in a falling drop and their relation to mass-transfer are complicated even further by film effects at the interface and by the possibility of chemical reaction within the liquid. Such effects are shown pictorially in Figure 3.5.

Surface film effects, which are expected to impede circulation within the drop and offer an additional resistance to mass transfer, depend in a compex way on trace impurities contained by the drop and upon specific interactions between the dissolving gas and the liquid. Chemical reaction in the liquid phase also may complicate the analysis enormously depending on the relative rates of mass transfer and chemical reaction. There are several reasons for this. The phenomenological expression for the rate of reaction may be highly complex — a problem that is compounded if several reactions occur simultaneously. Furthermore, chemical reaction usually violates the consecutive behavior exhibited by the mass-transfer steps of the process. In addition, it results in the formation of new species which subsequently mix and react further depending upon their own physical nature. Finally, because reaction rates often are related to concentration in a nonlinear fashion, the transport expressions cannot be evaluated reliably in terms of average liquid concentration as implied by Equation 3.2.

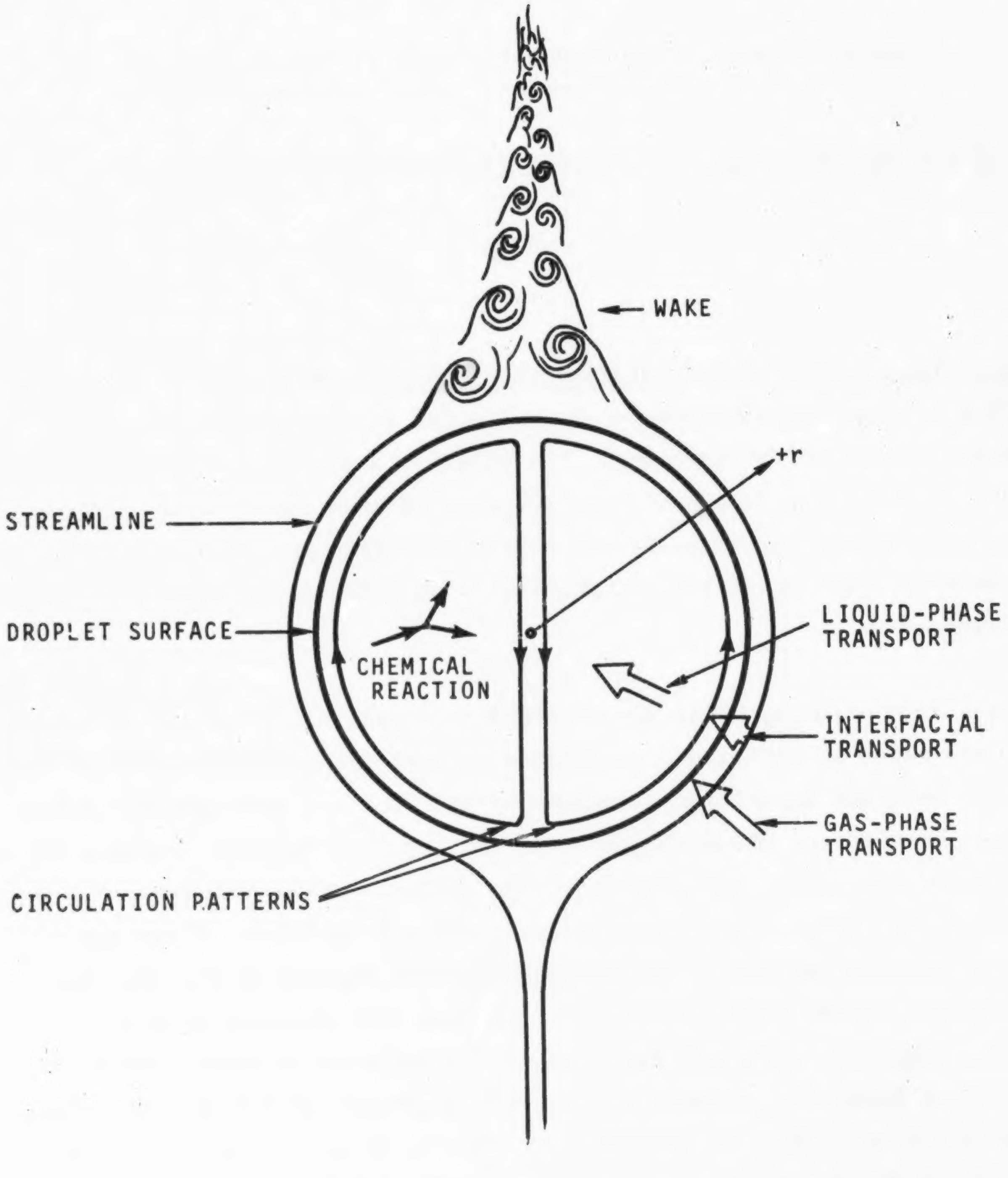
WAKE
+r
STREAMLINE
DROPLET SURFACE
CHEMICAL REACTION
LIQUID-PHASE TRANSPORT
INTERFACIAL TRANSPORT
GAS-PHASE TRANSPORT
CIRCULATION PATTERNS

Figure 3.5 Schematic of Transport and Washout Mechanisms in a Falling Drop

Obviously, such behavior is difficult to analyze mathematically. Because of the highly specific nature of these interactions, this behavior defies any generalized empirical approach similar to that employed for gas-phase transport. The remaining portions of this section examine the significance of each of the processes by considering first the problem of mass transfer inside a drop where neither chemical reaction nor interfacial resistance occur; the significance of these further complications then are considered in view of the more simplified behavior.

Liquid-Phase Mass Transfer in the Absence of Chemical Reaction -- A falling drop experiences frictional drag on its surface which tends to induce patterns of internal circulation (cf. Figure 3.5). Such circulation, combined with a variety of possible secondary mixing effects (e.g., oscillations and thermal perturbations induced by the drop falling through a temperature gradient), combine with molecular diffusion processes to effect a transfer of material within the drop. Such behavior is difficult to analyze theoretically; some insight to its significance, however, can be obtained by considering the two limiting cases of zero and infinitely-rapid convection within the drop.

For the case of rapid convection, the liquid mass-transfer coefficient becomes large. Equation 3.8 then reduces to

$$K_y = k_y \qquad , \qquad (3.21)$$

which can be evaluated using Equation 3.20. In the absence of irreversible chemical reaction, this behavior characterizes the most rapid rate of mass transfer possible, and establishes, therefore, an "upper limit" of behavior exhibited under atmospheric conditions.

For the case of zero convection, diffusion is the sole mechanism for transport. If the diffusion coefficient of A in the liquid, D_{Ax}, is known, the rate of transport in a drop can be determined by solving the appropriate forms of the continuity equation(16) for a binary mixture. Such solutions are given in the literature in terms of point concentrations within the drop.(24). These can be integrated over the drop volume to give

$$x_{Ab} = \frac{6D_{Ax}}{a^2} \sum_{n=1}^{\infty} e^{-\alpha t} \int_o^t e^{\alpha\lambda} \left(x_{Ao}(\lambda) - x_{Ai}\right) d\lambda + x_{Ai} \tag{3.22}$$

and

$$N_{Ao} = - \frac{2D_{Ax}c_x}{a} \sum_{n=1}^{\infty} x_{Ao}(t) - x_{Ai} - \alpha e^{-\alpha t} \int_o^t e^{\alpha\lambda} (x_{Ao}(\lambda) - x_{Ai})\, d\lambda \quad , \tag{3.23}$$

where

$$\alpha = \frac{D_{Ax}}{a^2} (n\pi)^2 \quad . \tag{3.24}$$

Equations 3.22 and 3.23 pertain to spherical drops initially containing mole fractions x_{Ai} of A, which is distributed uniformly throughout the drop interiors. Surface concentration x_{Ao} may vary with time in any prescribed manner. Simplified solutions for constant x_{Ao} and/or short exposure times may be obtained from the literature(24,25), or they may be deduced from Equations 3.22 and 3.23. In the absence of surface resistance, Equations 3.22 and 3.23 represent the slowest rate of mass transfer possible. These, therefore, combined with equations characterizing the rapid mixing case provide upper and lower limits for washout behavior. In the absence of irreversible reaction and/or surface resistance, all atmospheric washout behavior should fall somewhere between these two limits.

Nonlimiting behavior, as mentioned previously, is difficult to analyze. If circulation within the drops could be described exactly, one could attempt to derive and solve a binary continuity equation for the system and thereby predict N_{Ao}. Alternatively, one might employ the simpler but less exact technique of applying surface renewal and penetration theory.(26) Unfortunately, however, theoretical attempts to describe flow and mixing patterns within drops have met with somewhat limited success, a problem resulting from physical complications such as drop oscillation, turbulent flow, and nonidealities occurring at the gas-liquid interface.

For the case of small drops in the Stokes regime, (Re <<1), (cf. Figure 3.5), Hadamard(27) and Rybczynski(28), (cf., Levich(29)) have derived an equation characterizing drop circulation in the absence of vibration and surface nonidealities. Subsequently, Kronig and Brink(30) have formulated an idealized transport equation based upon the Hadamard-Rybczynski formula, and employed the solution to estimate mass-transfer rates. Kronig and Brink's solution, which depends upon the assumption that transport by circulation is rapid compared to that by diffusion, indicates that the liquid-phase mass-transfer coefficient is increased by a factor up to 2.5 if ample circulation is present. Most experimental results, however, indicate that for large drops this factor may be 10 or more(31,32,33) – a considerable deviation which has been attributed to increased mixing through oscillation of the drops as well as to extrapolation outside of the Stokes regime.

Surface phenomena also are expected to play a rather important role in complicating mixing behavior. Levich(29) employs the Hadamard-Rybczynski equation to demonstrate that when minute quantities of surface-active agent are present, this material is swept to the lee of the drop where it congregates and impedes further circulation. Surface agents also may cause changes in drop oscillatory behavior; implications of such interactions with regard to washout behavior in a contaminated atmosphere are obvious.

"Interfacial" resistance over and above that normally exhibited by the liquid phase may be an additional manifestation of surface-active materials within the drop. Such resistances have been measured experimentally for various surface-active agents in conjunction with the sulfur dioxide water system.(34,35) Because of the variety of possible types and quantities of agents occurring in natural rain, however, such results are almost impossible to utilize insofar as washout problems are concerned.

One should note that in the total absence of circulation, any film resistance decreases the liquid-phase mass-transfer coefficient to a value below that predicted by Equations 3.22 and 3.23, which was suggested previously as a lower limit. For most practical situations, however, net effects are such that K_y is larger than that predicted by Equations 3.22 and 3.23; hence these equations are employed to give some tentative idea as to the lower limit magnitude.

The considerable amount of additional work that has been published with regard to film effects and drop convection has been reviewed elsewhere (23,32,33) and is not considered further here. In view of the complexity of this problem, it is apparent that the success of any related analysis must depend rather heavily upon experimental measurements.

The Influence of Chemical Reaction -- Dissolution of gaseous sulfur dioxide molecules in water is accompanied by reversible chemical reaction. The absolute nature of this reaction has been the subject of some conjecture. Earlier it was supposed(36) that the scheme

$$SO_{2g} + H_2O \rightleftarrows H_2SO_3 \tag{3.25}$$

$$H_2SO_3 + H_2O \overset{K_1'}{\rightleftarrows} H_3O^+ + HSO_3^- \tag{3.26}$$

$$HSO_3^- + H_2O \overset{K_2'}{\rightleftarrows} H_3O^+ + SO_3^= \tag{3.27}$$

characterized true reaction behavior, K_1' and K_2' denoting equilibrium contants for the first and second ionization, respectively.

$$K_1' = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} \qquad (3.28)$$

and

$$K_2' = \frac{[H_3O^+][SO_3^=]}{[HSO_3^-]} \quad . \qquad (3.29)$$

Subsequent evidence(36) has indicated, however, that the compound H_2SO_3, "sulfurous acid," does not exist to any appreciable extent in water solution; rather, un-ionized molecules of dissolved sulfur dioxide appear to take the place of H_2SO_3 in Equations 3.25 to 3.29 to give the scheme

$$SO_{2g} + H_2O \rightleftarrows H_2O + SO_{2aq} \qquad (3.30)$$

$$SO_{2aq} + H_2O \overset{K_1}{\rightleftarrows} H_3O^+ + HSO_3^- \qquad (3.31)$$

$$HSO_3^- + H_2O \overset{K_2}{\rightleftarrows} H_3O^+ + SO_3^= \qquad (3.32)$$

where

$$K_1 = \frac{[H_3O^+][HSO_3^-]}{[SO_{2aq}]} \qquad (3.33)$$

and

$$K_2 = \frac{[H_3O^+][SO_3^=]}{[HSO_3^-]} \quad . \qquad (3.34)$$

Such evidence, which has been based largely upon various types of spectroscopic data, has indicated also the presence of trace amounts of the pyrosulfite ion, $HS_2O_5^-$, and various hydrates, $SO_2 \cdot nH_2O$. Other investigators,$^{(37)}$ however, cite vapor-pressure data to argue that H_2SO_3, or some related species, must be present in solution. At the present time, this conflict is not completely resolved, although the opponents of un-ionized sulfurous acid appear to have the bulk of evidence in their favor.

Most of the available experimental evidence suggests that the velocities of reactions 3.31 and 3.32 are rapid, although there are some indications to the contrary. Wang and Himmelblau(38) measured ionization kinetics of reaction 3.31 using a radioisotope technique and concluded that this reaction should proceed slowly, approaching completion on the order of one minute. Practically all of the evidence in the remaining literature is less quantitative in nature, but suggests that the results of Wang and Himmelblau are in error. Lynn and his co-workers,(39) for instance, measured the conductivity of a rapidly mixed solution of sulfur dioxide and water at various times following the initial mixing of the components, and found the ionization to be at least 90 percent complete in about 0.1 second. Toor and Chiang(40) obtained additional experimental data which indicated that these reactions should be essentially complete in 0.003 second, agreeing well with Saal's(41) earlier upper-limit value of 0.004 second for ionization reactions of this type. Thomas(37) argues that these measurements may have included some diffusion and secondary reaction effects which rendered these reaction-time estimates conservatively high.

Perhaps the most dramatic demonstration of the rapidity of the hydrolysis reactions is simply the rapid response of conductivity analyzers such as the Davis and the Sign-X, which depend upon these reactions for their operation. This is especially apparent with the Sign-X sulfur dioxide scrubber, which removes sulfur dioxide from gas streams by exposure to ion-exchange resin in water for extremely short residence times. If sulfur dioxide did not hydrolyze very rapidly, such scrubbers would be inoperable.

Whitney and Vivian(42) have suggested that hydrolysis times for sulfur dioxide in water may be somewhat greater than the preceding arguments indicate; but their analysis has been criticized subsequently by Lynn, et al.(39) who claim that the "reaction" effect apparent in their absorption data was probably caused by an inappropriate choice of a liquid diffusion coefficient.

The disagreement between the measurements of Wang and Himmelblau and those of the other workers is difficult to explain. From the description of the experiment given in their paper it appears that an undetected problem with sulfur dioxide partitioning to the gas phase as samples were withdrawn from their reservoir may have been a factor. This is purely conjecture and difficult to verify. Precipitation washout of sulfur dioxide, based on the validity of Wang's and Himmelblau's data, has been examined by Miller and DePena(43).

It appears that there is a need for further experimental work to resolve these questions, although it seems reasonable to analyze sulfur dioxide washout assuming rapid hydrolysis. Under such circumstances it has been suggested(44) that absorption can be treated as psuedo-physical phenomenon. The problem remains, however, of accounting for the multiple species formed by the reactions, each of which will diffuse at its own rate and recombine and/or dissociate depending upon conditions in its immediate environment.

For the limiting case of rapid mixing, such difficulties present no particular problem, since differences in molecular diffusion rates become unimportant and concentrations will be uniform throughout the drop. For the opposite limiting case, however, Equations 3.22 and 3.23, which pertain to a binary mixture, are not strictly applicable. A more elaborate set of equations, pertaining to conservation of species within the multicomponent system could be set forth. Because of their complexity and because of uncertainties of various physical properties, however, the value of such an effort is doubtful. It seems more expedient to choose a mean diffusivity and treat the sulfur dioxide water system as a pseudo-binary mixture to obtain estimates of the lower limes of washout behavior.

The complications of ionization reactions insofar as nonlimiting mixing behavior is concerned are obvious. To the authors' knowledge there have been no serious attempts to examine this behavior in detail theoretically.

In addition to the reversible, rapid ionization reactions that occur when a sulfur dioxide molecule comes in contact with water, slower, irreversible reactions may take place. Sulfate formation is undoubtedly the most important of the irreversible reactions, although many aspects of this formation process are not well understood at the present time. Junge and Ryan(45) have shown experimentally that trace amounts of catalyst in the drop influence reaction behavior strongly. Ammonium hydroxide, in addition to chlorine salts of manganese, iron, copper, and cobalt are active as catalysts for the oxidation. Sodium chloride, in contrast, appears to have little catalytic activity. For pure water solutions, Junge and Ryan found that sulfur dioxide oxidation takes place very slowly — behavior that has been observed also in this study.

Junge and Ryan noted that for a given ambient sulfur dioxide concentration, the rate of sulfate formation decreased with decreasing pH. Since sulfate formation results generally in a lowering of pH, this reaction tends to decrease in rate as it progresses, coming to a virtual halt at a pH of about 2. It has been suggested (cf., Scott and Hobbs(46)) that the observed retardation occurs simply because of the decreased solubility of sulfur dioxide under these circumstances; Junge and Ryan indicate, however, that a more complex type of autoinhibition may be involved.

Junge and Ryan point out that if a (chemically) basic material is present so that a suitably high pH is maintained, the sulfate-forming reaction will persist. These authors have demonstrated this experimentally using ammonium ion, a common constitutent of atmospheric precipitation.

Expressions for mass-transport rates to drops, wherein irreversible reaction occurs, are available in the literature for the previously described limiting cases(47,48,49). Such expressions, however, are often contingent upon the validity of Henry's law. In addition, these solutions have not dealt with the complications posed by variable catalytic activity and autoinhibition.

Previous experimental measurements(45) have indicated that rates of sulfur dioxide oxidation (half-lives of the order of hours) should be slow compared to rates of physical absorption as the drop falls through the rapidly changing concentration field of a plume. In view of such behavior, it appears permissible to neglect altogether the oxidation of sulfur dioxide under such circumstances, at least for situations wherein plume dimensions are not abnormally large, and the drops are sampled while still carrying a significant fraction of the sulfur dioxide collected enroute.

For circumstances wherein the time rate of change of sulfur dioxide concentration in the neighborhood of a drop is slow, the opposite may be true. That is, chemical reaction may be the most significant factor controlling the amount of sulfur dioxide being washed out. Such situations may exist for in-cloud washout or for cases of below-cloud washout involving long falls through regions where sulfur dioxide concentrations do not change rapidly. Estimations for washout of sulfur dioxide under such conditions have been published by previous authors(50).

ILLUSTRATIONS OF LIMITING WASHOUT BEHAVIOR -- The two "limiting" cases of washout behavior noted previously are characterized by Equations 3.8, 3.20, 3.21, 3.22, and 3.23. These cases are examined by calculating and comparing the washout rates predicted by both. One method of accomplishing this is simply to consider the rate of takeup (or loss) by a single drop falling in a region of known concentration. For simplicity, an initially clean drop is considered which falls through a region wherein the concentration is maintained at 1 part sulfur dioxide per million parts of air (PPM) ($y_{Ab} = 10^{-6}$). Subsequently, this same drop, now saturated with sulfur dioxide, is considered as it falls in clean air ($y_{Ab} = 0$).

Total transport to the drop may be found by integrating the flux expressions, Equations 3.1 and 3.2 with respect to time and multiplying by the drop surface area. This must be performed in conjunction with equilibrium data of the form given by Equation 3.6 using a trial-and-error procedure. The equilibrium relationship used here is based upon the data of Terraglio and Manganelli,(51) and is shown in Figure 3.6.

Mass-transfer coefficients for the various cases considered here are shown in Table 3.2. Here the gas-phase coefficients have been calculated from the Frössling Equation 3.20, and the overall coefficients were determined from Equation 3.5. Liquid-phase calculations are based on an assumed diffusion coefficient of 1.7×10^{-5} cm^2/sec(42).

Absorption-desorption curves based on these calculations are shown in Figures 3.7, 3.8, and 3.9. These curves are based upon rather idealized conditions of plume geometry, yet they illustrate vividly several points which characterize gas-washout phenomena. Perhaps, the most significant aspect illustrated by these curves is the ability of the drop to desorb gas under appropriate conditions. Thus, if a drop falls through a plume and emerges into cleaner air before reaching the ground, it may release a majority of the gas that is absorbed in more concentrated regions. Such behavior will tend to lower the altitude of the sulfur dioxide plume. The significance of this effect has not been investigated thoroughly; preliminary calculations indicate that, under extreme circumstances, it may be appreciable.

Figures 3.7, 3.8, and 3.9 show that the rates of absorption decrease toward zero as equilibrium is approached, a direct consequence of the

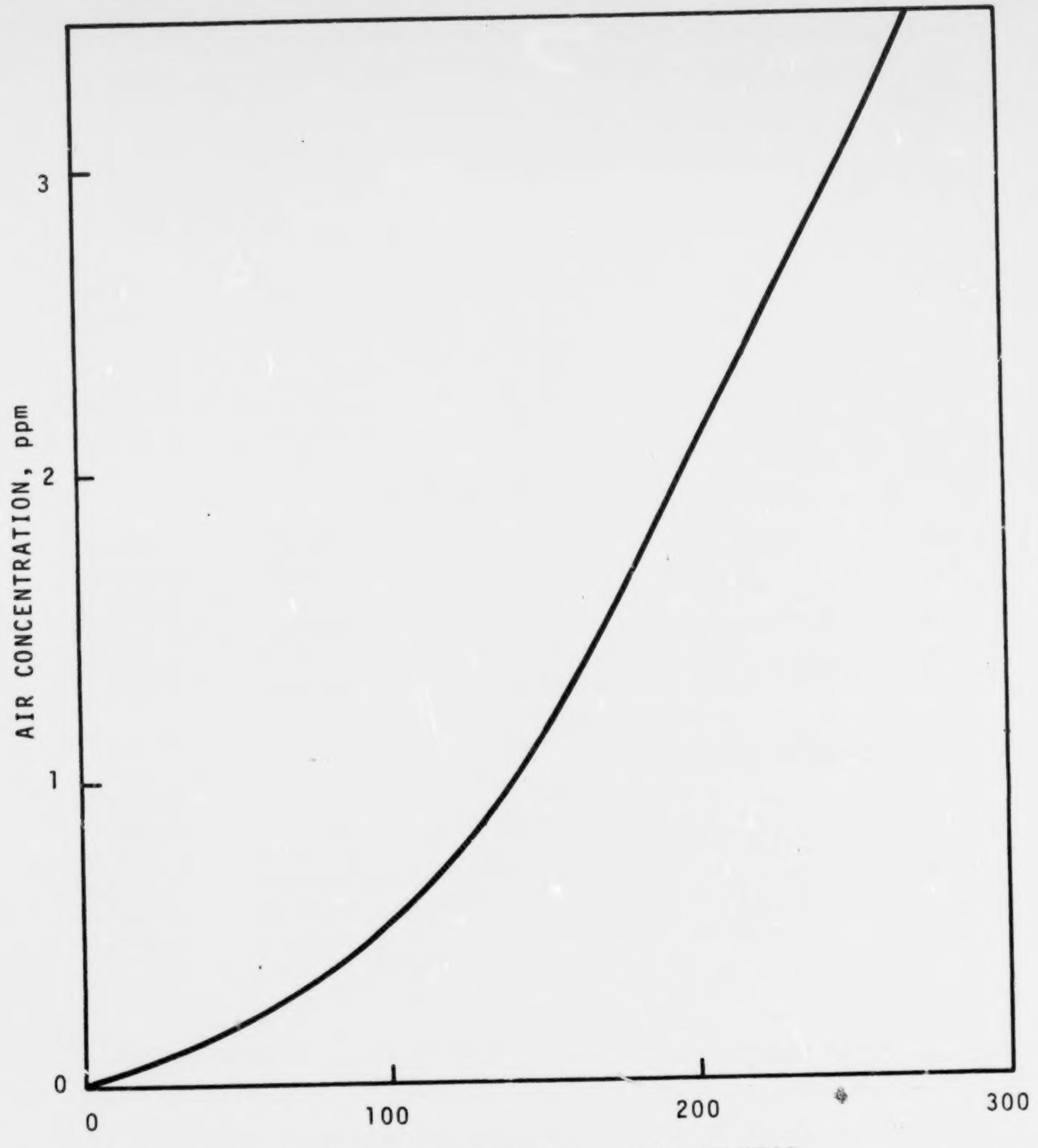

Figure 3.6 Equilibrium Behavior of the Sulfur Dioxide-Water System, Experimental Data for Moderately Low Concentration

TABLE 3.2

OVERALL MASS-TRANSFER COEFFICIENTS FOR STAGNANT FALLING DROPS

Fall Time sec	Liquid Concentration µmoles/L Absorption	Liquid Concentration µmoles/L Desorption	K_y Moles/cm^{2}sec Absorption	K_y Moles/cm^{2}sec Desorption
---- 0.3 mm Diameter Drop ----				
0.0	0.0	139.7	0.001258	0.001258
0.3	39.2	112.9	0.000475	0.000469
0.6	61.0	96.7	0.000389	0.000453
0.9	75.9	84.1	0.000322	0.000459
1.2	86.9	76.6	0.000280	0.000551
1.5	95.3	72.7	0.000246	0.000601
---- 1.0 mm Diameter Drop ----				
0.0	0.0	139.7	0.000891	0.000891
2.0	38.5	110.4	0.000212	0.000235
4.0	56.3	95.4	0.000152	0.000214
6.0	68.6	84.0	0.000126	0.000209
8.0	78.0	74.8	0.000110	0.000209
10.0	85.7	67.0	0.000099	0.000211
---- 3.0 mm Diameter Drop ----				
0.0	0.0	139.7	0.0000650	0.000650
20.0	53.1	93.8	0.0000715	0.000109
40.0	71.1	76.7	0.0000518	0.000101
60.0	83.3	64.4	0.0000437	0.000102
80.0	92.6	54.8	0.0000392	0.000105
100.0	100.0	47.0	0.0000364	0.000110

reversibility of the washout process. Such behavior points out the inapplicability for gas washout of the first-order irreversible model employed in most previous theoretical washout analyses. Contrary to assumptions employed in previous work,(52,53) the first-order irreversible model is not generally applicable for gas washout analysis even for situations involving trace-gases.

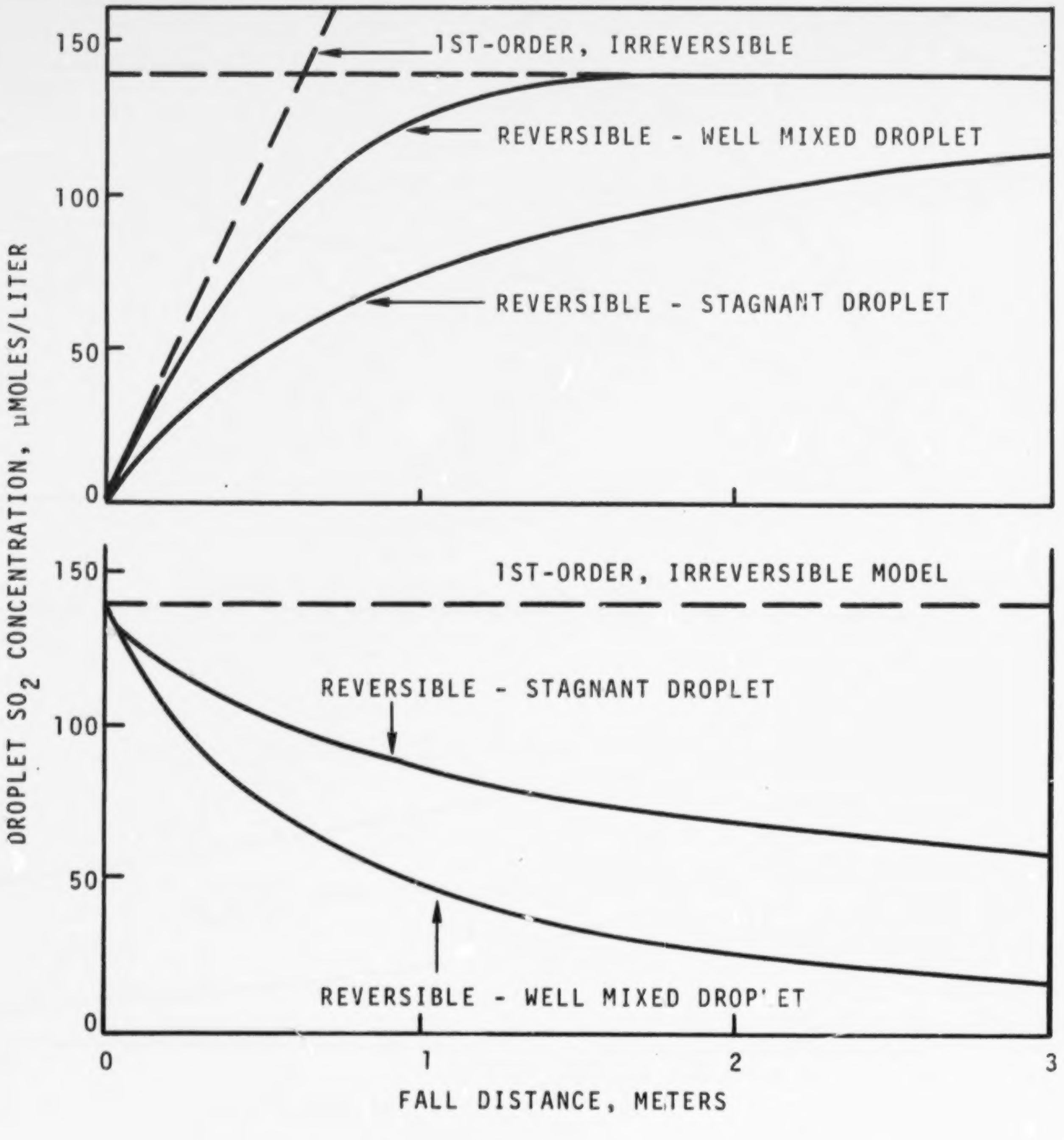

Figure 3.7 Absorption-Desorption Behavior for 0.03 cm Diameter Drops

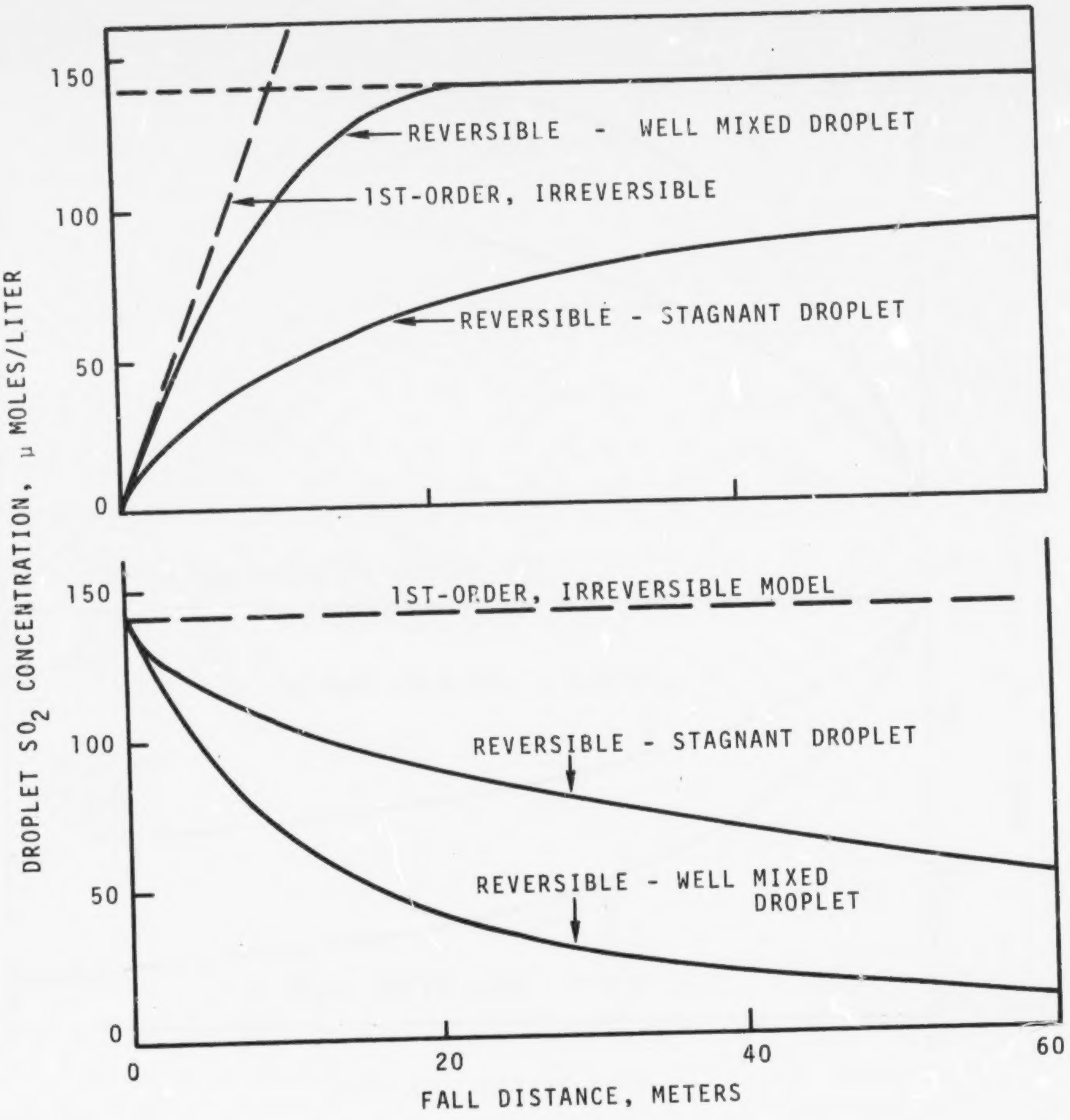

Figure 3.8 Absorption-Desorption Behavior for 0.1 cm Diameter Drops

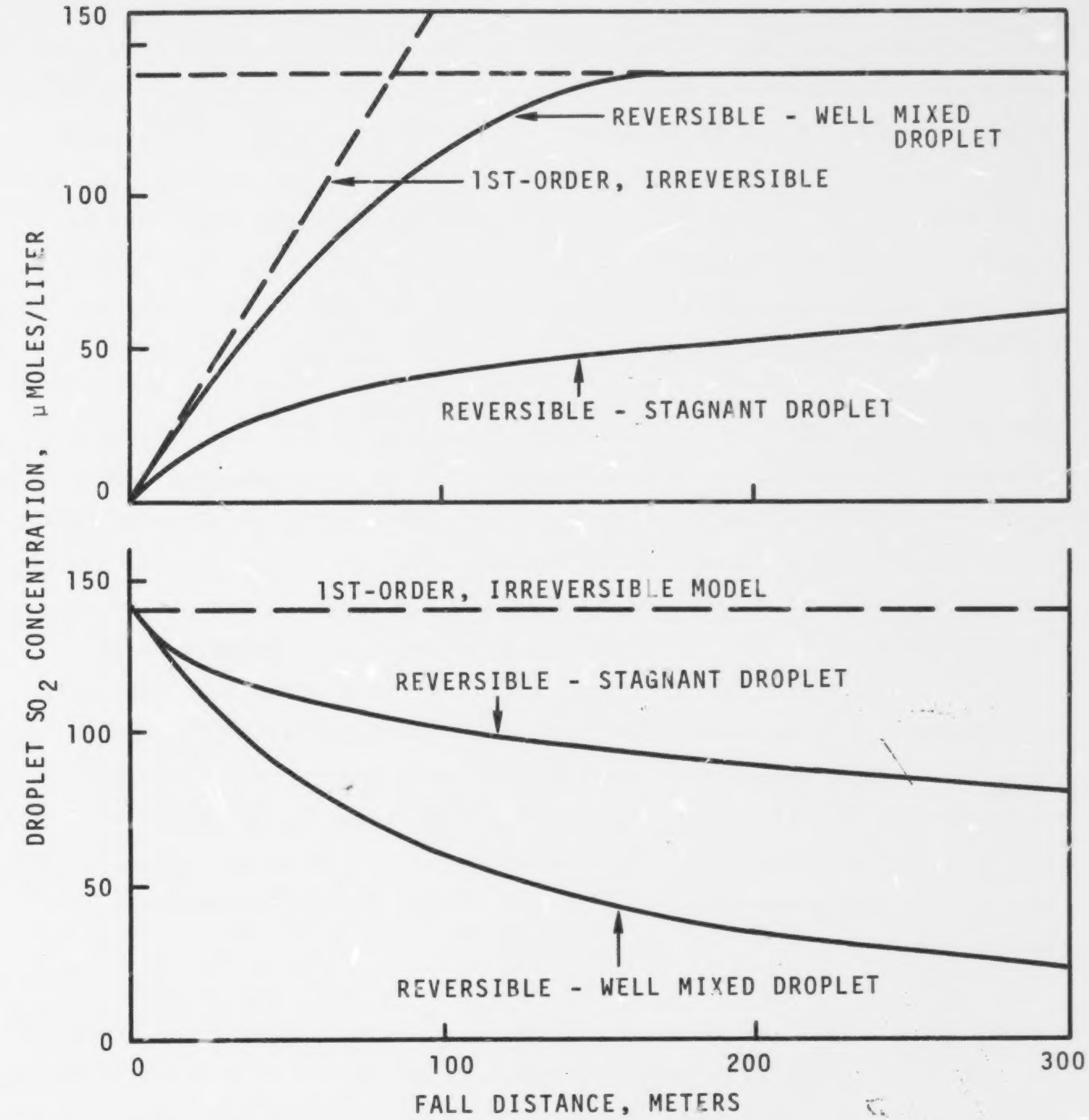

Figure 3.9 Absorption-Desorption Behavior for 0.3 cm Diameter Drops

Curves corresponding to the first-order, irreversible model are shown in Figures 3.7, 3.8, and 3.9 for comparison. From these, it is seen that application of the irreversible model for gases is valid only for conditions where the curves coincide. Such conditions might be approached for the situation of a small plume bordering the earth's surface; however, one would not expect these conditions to be valid in the present study. Inapplicability of the first-order, irreversible model is unfortunate in the sense that it invalidates, for most cases of gas washout, the more convenient method of analyzing washout behavior that was described in Chapter II. As a consequence, more physical data are required before a complete examination of the process can be performed, a fact that was indicated previously by Equation 3.19.

The upper and lower "limit" curves of Figures 3.7, 3.8, and 3.9, as discussed previously, bracket the behavior to be expected from real systems. Except for very large drop sizes, the limits of physical behavior are confined to fairly narrow regions, and, in a sense, these can be used as approximations in lieu of absolute knowledge of true behavior. "Patched" solutions of this type have been applied previously to other types of physical science problems.(54) In this context, the variation of the mass-transfer coefficient, as exemplified by Table 3.1, should be mentioned. From this table, one can determine limits for the overall coefficients and, if desired, estimate a mean value to be used for linearization in Equation 3.10. For cases wherein K_y varies widely, this mean should be chosen carefully in view of the physical conditions of interest.

An additional point concerns the sharp dependence of absorption behavior on drop size. In view of such behavior one would expect a dramatic difference in sulfur dioxide level between raindrops of different sizes, depending upon the history of the plume-raindrop interaction. Experimental field measurements of sulfur dioxide content as a function of drop size, not available at present, would be of high interest in this regard.

LABORATORY MEASUREMENTS OF SULFUR DIOXIDE WASHOUT -- The complexity exhibited by Equation 3.19 suggests that controlled laboratory experiments, rather than field studies, might be more effective in analyzing washout behavior theoretically. This equation is rewritten here for convenience.

$$Z = 4\pi N_T \int_0^\infty a^2\, f^*(a) \int_{C_a} \frac{K_y(y_{Ab} - y_{Ae})}{\bar{v}_a} \cdot d\bar{r}_a\, da + Z_o \quad . \qquad (3.19)$$

If, for example, experiments could be conducted with uniform drops falling vertically in air of uniform concentration, the integrals of Equation 3.19 could be simplified to

$$Z = \frac{4\pi a^2 N_T}{v_t} \int_{z_1}^{z_2} K_y(y_{Ab} - y_{Ae})\, dz + Z_o \quad , \qquad (3.35)$$

which reduces considerably the ambiguity involved in determining K_y.

Laboratory experiments in this area can be divided into four different categories, listed as follows:

1. Studies of drops suspended on solid supports.
2. Studies of drops suspended by moving gas.
3. Studies of isolated drops falling through gas.
4. Spray chamber studies.

Each of these types of experiments has its individual disadvantages. Studies of drops mounted on solid supports (e.g., hypodermic needles, filaments) have the strong disadvantage that natural circulation patterns are invariably perturbed. Such perturbations can be avoided with the second and third types of studies if care is taken to ensure that the newly formed drop is completely stablized in its environment prior to contact with gas. For the case of isolated, falling drops, this usually necessitates a long stabilization column, where the oscillations induced during drop formation are allowed to dampen out and terminal velocity is approached prior to contacting the gas. Some insight with regard to the effects of oscillations of newly formed drops can be obtained from the results of Garner and Lane(31).

Experiments involving single drops suspended in air have the serious disadvantage that, because of the inherently small sample size, they are not generally amenable to studies where low concentrations are involved. Isolated, falling drop studies overcome this disadvantage by combining several drops into one sample. Spray studies share this advantage; however, such experiments are plagued by several marked disadvantages, including unavoidable drop perturbation, nonconstant fall velocity, and the presence of a spectrum of drop sizes.

Experimental studies of the washout of trace sulfur dioxide by sprays have been conducted by Georgii and Beilke.(55,56) The above mentioned difficulties, however, have rendered these authors' results of limited value to the present study. Isolated falling drop experiments involving sulfur dioxide washout have been performed by Johnstone and Williams.(57) These studies, however, were confined to rather high sulfur dioxide concentrations and involved additive-containing drops. In this context, the suspended drop studies of Garner and Lane(31) should be mentioned. These studies also involved washout from gases of relatively high concentration.

The main use of the results of the studies described above is their common qualitative indication that both gas-phase and liquid-phase mass-transfer resistance are important in atmospheric sulfur dioxide washout. Further implications from these experiments of a quantitative nature are dubious insofar as trace-gas washout is concerned. Further data from an isolated, falling drop experiment would be of extremely high interest in this regard.

THERMODYNAMIC ASPECTS - CHEMICAL AND SOLUBILITY EQUILIBRIA

Solubility relationships, in addition to their importance in influencing transport behavior, are useful in estimating maximum and minimum washout rates in the absence of actual washout data. If the maximum concentration in a plume is known, for example, then one can state immediately that the concentration of washout gas in the precipitation is no greater than the equilibrium concentration corresponding to that maximum. Similarly, a lower limit can be established on the basis of the minimum concentration experienced by the drop, provided, of course, that there is no loss by reaction within the drop.

Dispite its importance to the understanding of sulfur dioxide washout, there is relatively little data pertaining to the solubility of trace concentrations of this gas in water. The bulk of sulfur dioxide solubility data that does exist pertains to higher concentrations than those of interest here. With the exception of some fragmentary information pertaining to air concentrations down to about 200 ppm, the only low concentration data that have been published are those of Terraglio and Manganelli, which were illustrated earlier in Figure 3.6.

Normal atmospheric sulfur dioxide concentrations are of the order of 0.01 ppm or less, and it is of interest to possess solubility data down through this region. Such information can be estimated roughly by extrapolating the existing data to the concentration levels of interest, provided that certain assumptions with regard to equilibrium behavior are made. On the basis of previous work(58) it appears justifiable to assume Henry's law to be valid for the equilibrium between gaseous and aqueous molecular sulfur dioxide (Equation 3.30). Thus

$$[SO_2]_g = H[SO_2]_{aq} \tag{3.36}$$

On the basis of available data, $H \approx 1.0$ at 20°C, provided $[SO_2]_g$ and

$[SO_2]_{aq}$ have units of ppm and μmoles/l, respectively.

Previous work indicates also that the second dissociation constant is so small that it can be neglected for all practical purposes. From this work, one may estimate the first dissociation constant, K_1, to be about 1.7×10^4 μmoles/l at 20°C.

Two types of hydrogen ion may exist in the solution, that arising from the ionization of sulfur dioxide and that originating elsewhere (e.g., from the presence of dissolved sulfate). It is useful to differentiate between these; the latter will be referred to as "excess" hydrogen ion. Thus,

$$[H_3O^+]_{TOTAL} = [H_3O^+]_{SO_2} + [H_3O^+]_{ex} \quad . \tag{3.37}$$

Combination of Equations 3.33, 3.36, and 3.37 provides an expression for c_{SO_2}, the total concentration of dissolved sulfur dioxide:

$$c_{SO_2} = [SO_2]_{aq} + [HSO_3^-]$$

$$= \frac{[SO_2]_g}{H} + \frac{-[H_3O^+]_{ex} \pm \sqrt{[H_3O^+]_{ex}^2 + 4K_1[SO_2]g/H}}{2} \quad . \tag{3.38}$$

Solutions to Equation 3.38 are plotted in Figure 3.10. Here the parameter denoting "excess pH" is simply the pH arising from the presence of excess hydrogen ion, i.e.,

$$\text{excess pH} = -\log_{10} 10^{-6}[H_3O^+]_{ex} \quad . \tag{3.39}$$

The curves of Figure 3.10 indicate a rather strong dependence of solubility on pH. Such dependence is important for a number of reasons, Firstly,

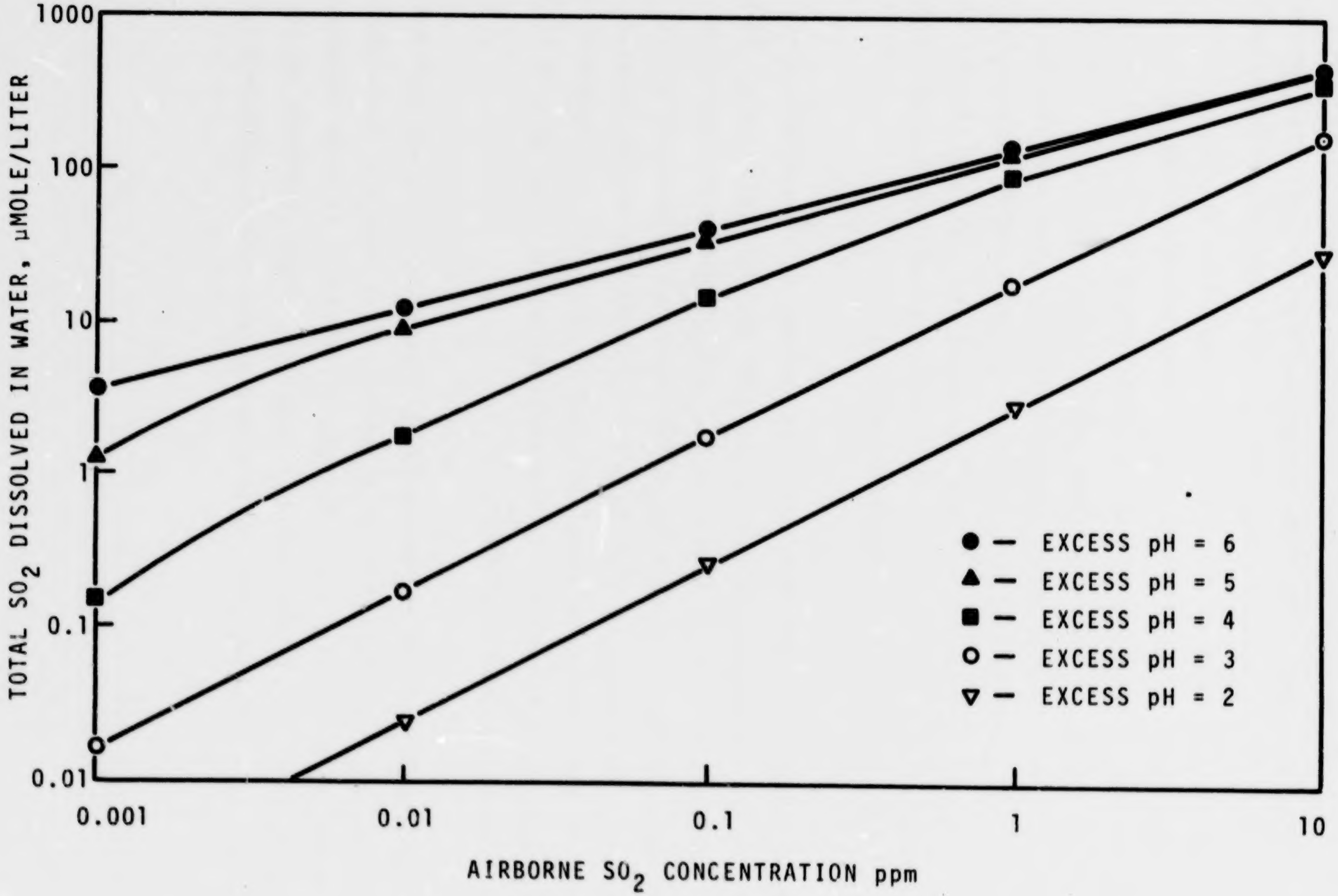

Figure 3.10 Estimated Solubility of Sulfur Dioxide in Water

this would lead one to expect a general lowering of measured washout rates with decreasing pH. Secondly, this dependence would be expected generally to decrease the effectiveness of washout in the plume, since the plume itself contains acid-forming material (e.g., sulfates, nitrates) which will be washed out and serve to lower pH. Such an effect explains the otherwise paradoxical situation where sulfur dioxide concentrations in rain that has passed through the plume are actually lower than those in rain that has not. This phenomenon is suspected to have contributed significantly to behavior exhibited by much of the data of this study. Since pH lowering by washout in the plume should be more significant the higher the pH of the incoming rain, this effect should be more pronounced under circumstances wherein background pH is high.

Finally, it should be noted that in-plume washout of acid-forming materials complicates the calculation of sulfur dioxide washout enormously. Referring to Equation 3.5, it is seen that the equilibrium relationship is no longer fixed, but varies with time as the acid-forming substances are accumulated. This suggests that in order to calculate sulfur dioxide washout, one must have substantial information pertaining to washout of other atmospheric species, making any thorough analysis under such conditions a truly formidable problem.

It is emphasized that the arguments of this section are based upon extrapolated data, the accuracy of which is rather questionable. Experimental measurements of solubility as a function of excess pH in this concentration region would be of high value in examining these phenomena in further detail, and in validating the implications of the present discussion.

CHAPTER IV

REVIEW OF FIELD EXPERIMENTS

Chapter IV contains an overall review of the field experiments. The primary data — concentrations of sulfur dioxide recovered in the precipitation collectors — are tabulated in Appendix A. Graphical representations of sulfur dioxide distributions on the grid are included there also. On these, concentrations are represented by radial bars of proportionate length extending from the collector locations. Vertical profiles of wind velocity, determined principally from pibal soundings at the Overlook, appear in Appendix A to account, in part, for the observed distributions.

Run data in Appendix A are grouped according to the experimental period in which the run was conducted. A table preceding each group summarizes the runs relative to the operations, wind velocity, precipitation rate, sulfur dioxide emission from Keystone, and sulfur dioxide recoveries on the grid.

Frequent reference is made to the data of Appendix A throughout this chapter.

REVIEW OF FIELD EXPERIMENTS

Experimental runs were conducted during three separate periods of approximately one month duration: October-November, 1969; February, 1970; and April-May, 1970. Autumn and Spring runs were conducted in rain and the Winter runs all were conducted in snow. The Spring runs were added to the program because of a particularly dry Autumn.

FIELD PERIOD 1 -- The first three weeks of the Autumn period were characterized by warm, clear weather, which provided ample time for preparation for field experiments, but delayed the initial experiment to test the adequacy of those preparations. The first run was conducted at night on October 20 and the final four runs occurred on the mornings of November 1 and 2.

Autumn rains were accompanied by low clouds, which resulted in insufficient ceilings for aircraft operation during four of the five runs. The one occasion for which aircraft use was possible provided an opportunity to develop aircraft sampling capability under experimental run conditions. All equipment operated satisfactorily, resulting in the measurement of temperature, humidity, and sulfur dioxide concentration from near stack height to cloud base in traverses about one mile downwind of the Keystone Station.

It was planned that definition of the stack plume geometry would be provided photographically. However, the plume is not normally visible, except for condensation of its vapor, because of the highly efficient removal of fly ash by the electrostatic precipitators. When conditions are proper for persistence of condensate in the stack plume, it normally is obscured by the cooling-tower condensate plumes.

Pibal soundings showed that the wind direction varied widely with height; in one case, exceeding 100° within 2000 ft. This questioned the adequacy of sampling on 90° of arc, since a wider distribution of sulfur dioxide in precipitation must be assumed with such large directional shear. Consequently, the sampling arcs were extended during the later experimental periods.

Subsequent analysis of the first period data showed sulfur dioxide concentrations in the collectors to be distributed erratically. Neither a quasi-normal distribution along the arcs, nor a decrease in concentration with distance was evident. Wide variability between adjacent collectors and alignment of troughs on one arc with peaks on the other were common. Large differences between peak and background generally were not observed. The absence of reduced values at the extremes of the arcs suggested that the plume had not been contained.

Expansion of the grid with sampling to a greater distance and increased lateral coverage was deemed necessary to contain the plume and document the possible increase of concentration with distance. Both actions were taken in Field Periods 2 and 3. The reduced likelihood that meaningful correlation of washout and precipitation characteristics could be achieved, due to the wide variability in washout, resulted in conducting precipitation characterization at only one location during the subsequent periods. Precipitation charge spectra were taken infrequently and no attempt at their correlation with washout has been made.

Run 1 -- Deployment of the precipitation collectors began in moderate rain following the passage of a thunderstorm which occurred about two hours ahead of its forecast. Less than half were in position when the surface wind measurement at the Overlook showed a shift from 280° to 250°. The wind shift was accompanied by a sharp decrease in rainfall intensity, and a number of collectors deployed on the southern portion of the arcs after this time received insufficient precipitation for analysis.

The fact that the collectors, which sampled the heavier rainfall during the period when the surface wind direction placed the plume south of them, did not give evidence of dilution leads to the conclusion that only the surface wind exhibited a northerly component. Both the 1900 EST Pittsburgh sounding, which showed a wind direction of 230° near the stack height elevation, and the 240°-250° winds measured at the Overlook following the weather disturbance suggest that the upper winds were west-southwesterly throughout the run.

Figure A.2 and Tables A.2 and A.3 show significantly lower concentrations beyond Stations A-17 and B-16, which were installed following the surface wind shift at 2140 EST. Exceptions to this are Stations A-26 and B-17, whose very high values are attributed to the exhaust of gasoline-powered generators at those locations. High readings which appear at A-21, A-22, A-25, B-20, B-21, and B-24 are unexplained, but may be due to unobserved surface winds which retained their northerly component after the wind shift.

An alternative explanation of the observed distribution is that the washout sulfur dioxide was derived from an upwind source which blanketed the entire grid. This would result in a fairly homogeneous background distribution and, supposedly, the Keystone plume washout would be superposed upon it. It might be argued from the distributions shown that no addition to the background is obvious and that a deficiency is more likely. The discussion of subsequent runs will also note this apparent negative influence of the Keystone plume.

Run 1 pointed up several deficiencies in the experimental design. Whereas this method of sampling had been used successfully in small-scale experiments, a more complex situation exists on this larger scale. Wind shear, for example, becomes an important problem when a buoyant plume is emitted from an 800 ft stack. The necessary grid size to investigate the release of sulfur dioxide from a tall stack introduces the problem of sufficiently rapid collector deployment and retrieval to attain concurrent sampling at all stations and assure plume containment throughout a run.

Runs 2, 3 -- Runs 2 and 3 were conducted on a morning of warm front precipitation and a cloud base sufficiently high for aircraft operation during Run 2. The aircraft traverses from 2000 ft to 3000 ft MSL showed sulfur dioxide at all levels in peak concentrations of 1-4 ppm. The temperature lapse rate was only slightly stable — 2.4°C/1000 ft — and was conducive to the observed mixing at this time. Orientation of the intercepts of sulfur dioxide from the Keystone stack was along the wind direction shown by the pibal sounding at 0725. At all levels, the wind was between 165° and 170° at that time.

The surface distribution of sulfur dioxide in the collectors, Shown in Figure A.4, indicates a minimum concentration on Arc A at a bearing of 330° to 345° from the Keystone stack. Larger values lie to the north, beneath the aircraft intercepts of the plume, and also to the south. Washout concentrations on Arc B do not show a similar dip, but increase generally from south to north. The dip in concentration on Arc A may be the result of plume splitting at the stack which is discussed in a later section.

It is unlikely, under the observed wind profile, that the sulfur dioxide distribution from north to north-northeast of the Keystone Station originated at Keystone. It is suggested that the source of this distribution was the Homer City Generating Station, which is appropriately oriented some 12 miles further upwind, as shown in Figure 4.1. One measurement of sulfur dioxide by the aircraft in a traverse at 2500 ft which extended north of the other traverses was apparently due to an intercept of the Homer City plume.

The absence of washout sulfur dioxide north of Keystone in the Run 3 distribution, shown by Figure A.6, is due to the termination of the rain before northern portions of the arcs were deployed. The higher concentrations to the west of Keystone are a result of continued backing of the winds with time at increased heights as shown by the 0930 pibal in Figure A.3.

Runs 4, 5 -- Rainfall was heavier and the overcast thicker and lower than on the preceding day when Runs 2 and 3 were conducted. Aircraft operation was not feasible. Run 4 was conducted during a period of heavy precipitation with the rate exceeding 9 $\mathrm{mm\text{-}hr^{-1}}$ for a brief period when all collectors were positioned. The storm had nearly passed before the change-out of collectors had been completed for Run 5. Throughout the morning, the raindrops were quite uniform in size at about one-half millimeter diameter. The air was near saturation.

Approximately 90° of shear was shown by the pibal sounding during Run 4 with directions ranging from east-northeast at the Overlook to south-southeast about 1000 ft above the stack exit. Wind speeds were lighter than on the preceding day and the buoyant cooling tower plume was observed to interact with the stack plume.

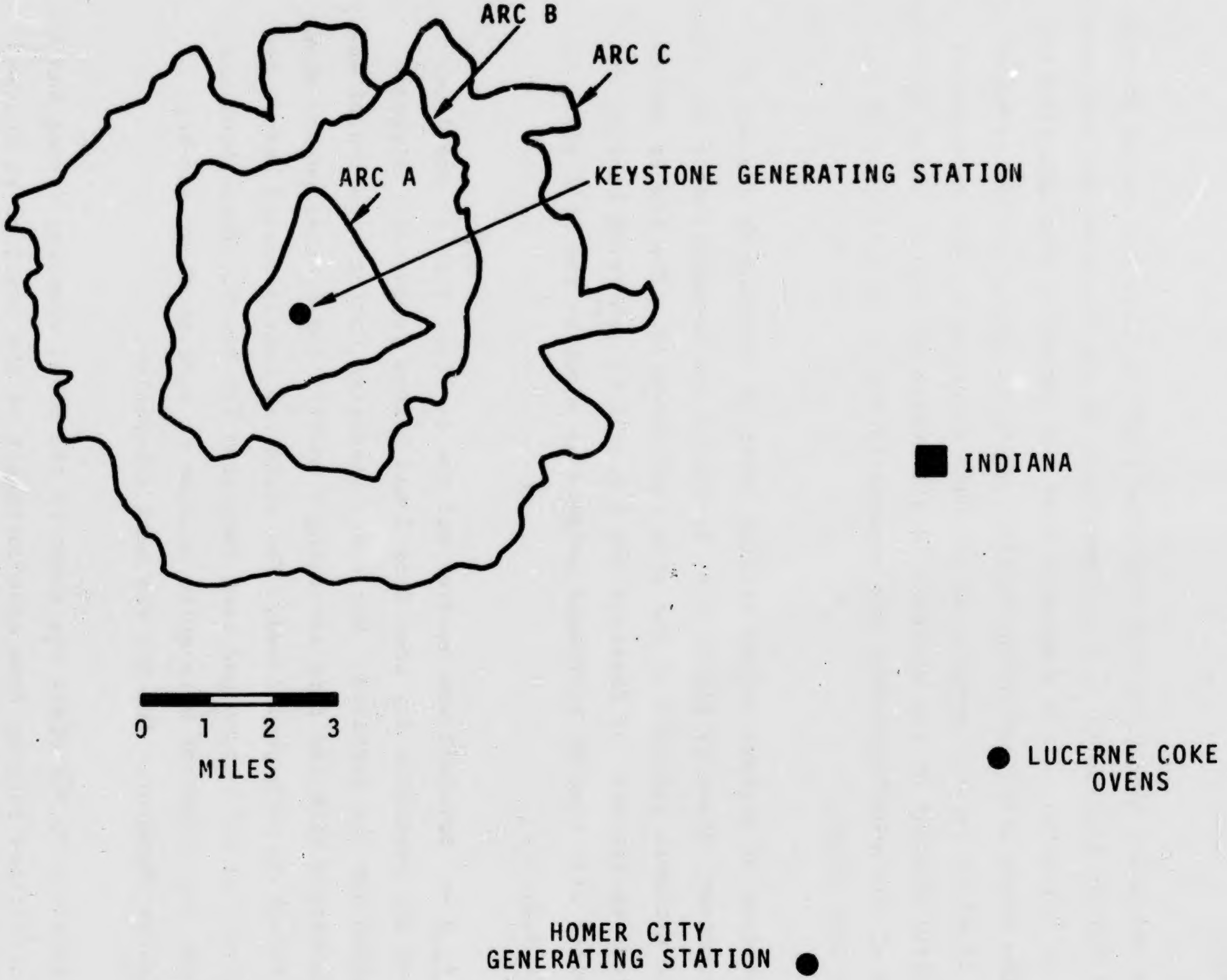
ARC B
ARC C
ARC A
KEYSTONE GENERATING STATION
INDIANA
0 1 2 3
MILES
LUCERNE COKE OVENS
HOMER CITY GENERATING STATION

Figure 4.1 Keystone Area Map

Based upon the observed winds, containment should have been nearly complete, but high values at the arc ends make uncertain the degree of containment. During the period of the runs, observed winds had insufficient directional range to account for the distribution at the arc extremities. Clearly, the winds were suitable to transport the Homer City plume over the arcs. This apparently is the source of much of the observed washout sulfur dioxide, since the Homer City furnaces were fired throughout this day.

Lower volumes of collected rainfall on Arc B in Run 5 are the result of decreased rainfall rate before complete deployment of that arc. Total sulfur dioxide recoveries on Arcs A and B were essentially equal for Run 4. Since concentrations also were comparable on the two arcs, this points up the general contamination of the entire sampled grid.

One feature which was quite prominent in both runs is the decrease in concentration on Arcs A and B beneath the expected plume path. In fact, a line through the troughs exhibits a curvature suggestive of the veering wind. Unlike Run 2, this low concentration region cannot be accounted for by splitting of the plume since there is little evidence that adjacent, high concentrations can be attributed to the Keystone plume. It appears, therefore, that the Keystone Station actually had a negative effect on washout in this instance. It was also noted that minimum sulfur dioxide values were associated with maximum sulfate values and this is discussed in Chapter V.

FIELD PERIOD 2 -- Suitable weather for experimentation in snow occurred only during the first half of February. Seven runs were made in a variety of snow situations. Again, the distributions of sulfur dioxide concentration in the precipitation were erratic. The apparent lack of plume containment by the samplers, which was indicated in the first period, was again noted, but general obscuration of the plume washout by the washout of background sulfur dioxide now was considered a more likely explanation, since sampling arcs had been extended.

Along with the extension of the sampling arcs, field procedures were altered to provide shorter duration for deployment and retrieval of precipitation collectors. Ideally, the sampling should be concurrent at all collectors during a run to minimize the effect from variations in precipitation with time. An extended period for change-out between consecutive runs further complicates the analysis since sampling on the first run is continuing while sampling on the second run is beginning. Two or three crews of two men each were used for deployment and each arc was deployed in turn. This was in contrast to the first period operation when two men concurrently deployed both arcs. Despite extension of the arcs by 100 percent and the addition of 50 percent more collectors, the time was cut significantly. The difference between the average total sampling duration for each collector and the concurrent sampling duration for all collectors was reduced from 52 minutes during the first period to 26 minutes during the second period. Additional manpower was made available by the reduced emphasis on precipitation characterization and as a result of the inability to use the aircraft during low ceiling and low visibility conditions in snowfall.

Photographic documentation of snowflake characteristics was provided for each run of this period through the use of special equipment. Snow conditions differed on the four run days and these differences are clearly shown in the photographs which are discussed in Chapter V.

Run 6 -- The first run in the snow washout series was conducted during a moderate snowfall. The 0700 EST Pittsburgh sounding showed a weak inversion extending to about 2000 ft above the surface, indicating a very stable air mass. Surface temperatures were 15°-20°F during the run and the snow consisted of small, dry grains and crystals. Surface winds were west-northwesterly and the Pittsburgh rawinsonde showed north-northwesterly winds aloft. Pibal soundings and other support operations were not provided as a consequence of the occurrence of suitable experimental weather less than a day after crew arrival in Pennsylvania.

Approximately 189° coverage was provided on Arcs A and B. Primary collectors, those for sulfur dioxide and sulfate, were spaced at double the interval used during the first field period. Secondary collectors were located at alternate primary collector stations to provide samples for pH, nitrate, and nitrite analyses.

The distribution shown by Figure A.12 exhibits a multimodal character and is seen to be quite erratic. Distributions at the northeast end of Arcs A and B and at the southwest end of Arc A are believed to be unrelated to the Keystone emission considering the existing wind regime. All of these collectors were located in narrow road cuts or along steep hillsides which under the existing conditions of flow and stability might tend to concentrate vehicle exhaust and sulfur dioxide from other sources in the vicinity of the collectors.

The plume appears to have been contained, particularly if the outliers can be ignored. A further indication of containment was a visual observation from Arc B during the run which placed the plume near the center of the arc. This position was aligned along the near-surface wind direction. It is suggested that the second mode, south-southeast of Keystone, was associated with the upper level winds. As in Run 2, there is a suggestion of plume splitting at the stack, which permits two distinct areas of washout. Additional support for this phenomena is given in a later section.

Runs 7, 8 -- Precipitation on the day of Runs 7 and 8 was quite heavy and relatively steady. However, Tables A.15 through A.18 show large variations between collectors in the volumes of precipitation collected. This is a problem common to all precipitation samplers because of local wind speed variations. It is more pronounced for snow because of its low terminal velocity and the degree of reentrainment. Consequently, the effective area of the collector is reduced by high wind and increased by drifting snow. It is probable that the large volumes collected were the result of drifting snow.

Wet amorphous clusters of snow were mixed with light rain and surface temperatures remained above freezing during Runs 7 and 8. The air was near saturation and moderately stable. A pibal sounding in the morning showed a wind direction of 138° near the surface, veering to 178° at approximately double the stack height.

The arcs which were centered north-northwest of the Keystone Station provided about 180° coverage. Collector spacing was the same as on the preceding run and secondary collectors were used in a like manner. The extent of coverage in relation to the observed winds should have ensured plume containment. In addition, three separate sightings of the plume from the arcs placed it northwest of Keystone, yet the distributions, shown in Figures A.14 and A.16, extend over all sampling positions on both arcs. If any evidence of the plume exists to the northwest of Keystone, it is an apparent decrease in concentration as noted previously with south-east flow.

Both units at Homer City were operating on this day, and it is apparent, therefore, that washout from the Homer City plume obscured the Keystone washout. All collectors were downwind of Homer City based on the observed winds. The sulfur dioxide contained in collectors on the northeast leg of Arc A was due, probably, to washout from the Homer City plume. Maximum values of about 10 μmole-liter^{-1} are attributed to this source at a distance of about 13 miles.

Runs 9, 10, 11 -- Temperatures were slightly above freezing at the surface and the 0700 EST Pittsburgh sounding showed below freezing temperatues aloft, so that all precipitation fell as snow. The air was saturated and the ceiling was 500 ft, or less. Following Run 11, a pibal was tracked to stack height, but previous pibals were tracked only 30 seconds due to the low ceiling. All observed winds were between 270° and 290°.

The indicated winds were westerly at the surface, with speeds increasing through the day. Higher elevation winds were poorly defined even on a regional scale since Pittsburgh's wind soundings were not complete and the morning pattern throughout the eastern seaboard was poorly defined. Northerly flow in western Pennsylvania was the most probable at lowest elevations, though northeasterly could not be ruled out. Within the first 2000 ft above the surface, easterly and southeasterly winds also were indicated prior to noon. The sulfur dioxide distributions of Figures A.18, A.20 and A.22 fail to provide indication of a preferred wind direction, though Arc A was completely sampled in Run 9.

As indicated by collector volumes, the precipitation was quite uniformly distributed on Run 9, but became somewhat erratic later in the day with increased wind speed. Washout patterns were quite similar for these three consecutive runs, but concentrations were noticeably lower on Runs 10 and 11. This was due perhaps to the increased wind speed, which decreased the airborne concentration by stretching the plume.

The uniformity of sulfur dioxide distribution again points to a source other than the Keystone Station, but the poorly defined wind field makes the source unidentifiable. Low sulfate measurments shown in Tables A.20, A.23, and A.24 suggest that the background air was clean. Based on the observed near-surface winds, the air previously passed over open farmland. It should be noted also that sulfate concentration peaks were found at Stations B-22 and B-26 in Run 9 and A-18 and A-20 in Run 11. These stations are downwind of Keystone based on the observed winds. Sulfur dioxide concentrations in collectors B-22, B-24, B-26 of Run 9 and A-18 of Run 11 had the lowest values. This relationship between sulfur dioxide and sulfate concentrations which was observed in Runs 4 and 5, also, is discussed further in Chapter V.

Run 12 -- Arc B alone was employed in this run, which sought to contrast the Keystone plume with the background for an unambiguous wind flow. Pibal soundings showed the winds veering from east-southeast near the surface to south-southeast beneath the inversion base indicated at 2500 ft MSL on the 1900 EST Pittsburgh sounding. The Pittsburgh sounding also showed neutral stability in the layer below the inversion. Surface temperatures were below 20°F and temperatures above freezing showed nowhere in the sounding. Light precipitation fell as crystalline snowflakes.

The sulfur dioxide concentrations in the collectors were low, as they had been in Run 6. Unlike that run, the distribution consisted largely of washout from sources other than Keystone. The broad distribution along the southern portion of Arc B could not have originated at Keystone with the observed winds. The Keystone plume was observed over Arc A at a bearing of 300° from Keystone and the peak value for the entire arc, as shown in Figure A.24, corresponded with this observation and with the stack height wind direction.

Two factors appear to rule out Homer City as the source of washout south of Keystone. On the basis of washout during prior runs on the arcs, Homer City contributes significantly higher concentrations than Keystone and this would certainly be the case during Run 12 when both units at Homer City were operational. The concentrations south of Keystone, however, are about equal to the peak concentration northwest which is attributed to Keystone. Also, for Homer City washout to be evident on the southern portion of the arc, it would also be evident on the western portion with which it is aligned.

The probable source for the washout south of Keystone in Run 12 is the coke ovens which are located at Lucerne, south of Indiana. This source is shown in Figure 4.1. The highest concentrations on the arc south of Keystone lie at an azimuth of 290° from Lucerne. It is interesting that this source, which is located at a distance of over 8 miles, contributes as much sulfur dioxide washout on Arc B as the Keystone Station at a distance of 2 miles. Assuming that the release rate of sulfur dioxide from the coke ovens is well below that of Keystone, the increased surface air concentration from this surface release must be a significant factor.

FIELD PERIOD 3 -- Precipitation during April was more evenly distributed than during the previous two periods, although appreciable rain fell on only three days. On one of these days, three runs were conducted; the first during passage of an isolated cell, and the last during passage of a vigorous cold front. Large differences in the sulfur dioxide washout were observed between these runs.

An innovation during the April period was the use of the sulfur dioxide analyzer, which was intended for use in the aircraft, for sampling of the near-surface air. It was mounted on a truck and driven on the arcs to locate high concentrations from the Keystone Station and other sources. These tests are described in a later section.

Arc C, which had been installed during the February period, was utilized in four of the April-May runs, Arc B in three others. A dry run to evaluate the collector response to sulfur dioxide air concentration was also made. In addition, one intended run, Run 17, failed to receive precipitation, and another, Run 13, received such small amounts as to be unsuitable for further consideration.

Support equipment was sparse as a result of a wildcat Teamster strike when the equipment was in transit.

Runs 14, 15 -- Heaviest sulfur dioxide recoveries were realized on Runs 14 and 15 which were conducted under an easterly wind flow. Winds prior to Run 14 were east-southeast at all levels. Throughout the morning, the winds backed so that by the end of Run 15 they were essentially from the east, the final pibal showing lower elevation winds with a northerly component and upper winds with a southerly component. Wind speed increased significantly above stack height though this may have been only apparent — due to the heavier, wet pibal. The air was essentially saturated throughout a deep layer from the surface and the thermal stability was about neutral.

Moderate precipitation was quite steady over the entire grid. The synoptic map, in fact, showed precipitation was widespread northwestward from an intensifying storm system near Norfolk, Virginia.

The distributions of sulfur dioxide shown in Figures A.26 and A.28 fail to define the plume clearly at a direction of 280° from Keystone as visually located by an observer on Arc B. The sulfur dioxide distribution, which obviously was derived from a source other than Keystone, could not have been associated with Homer City under the existing wind regime. Although the city of Indiana lies immediately upwind of Keystone, distribution over the entire grid at a near-constant concentration suggests a more distant source or more diffuse sources; the latter explanation is preferred. A single source would necessarily be very distant considering the apparent directional constancy of the wind. Travel over a long distance likely would diminish the sulfur dioxide content of the air mass by conversion to sulfate. However, the sulfur dioxide concentration in the precipitation was high and the sulfate content was low. A number of minor domestic sources undoubtedly were available throughout the area since temperatures on this day were about 45°F.

Given the information that the Keystone plume was visually located 280° from the source, evidence of washout was sought in the sampling data. Maximum sulfur dioxide concentrations were found in Run 14 at Stations B-62, B-64, and B-66, which lie between 260° and 275°. Again in Run 15, the maximum on that portion of the arc is found at Station B-64. If these are indeed evidence of the Keystone plume, the washout from it is about 3.5 to 5.0 μmole-liter^{-1} and constitutes 20-25 percent of the total.

Run 16 -- Run 16 was the first to utilize Arc C. Although the day looked promising for precipitation, the 0700 EST Pittsburgh soundings showed only a thin saturated layer at 10,000 ft. It also showed moderately stable air below stack height and an inversion above it. Most of the rain fell in a half-hour period during collector deployment so that not all collectors received sufficient amounts for analysis. Winds during the major rain period were easterly near the surface and veered to southeast about 2000 ft above the surface. At still greater heights, probably above the inversion, winds veered through south to west-northwest.

Figure A.30 shows the washout sulfur dioxide distribution. The clustering of concentration measurements reflects the short period of rainfall, since the collectors shown are those which each team deployed before the rain terminated. Maximum concentrations south of Keystone can be attributed either to Homer City or to the Lucerne coke ovens depending on whether the stack height or surface winds are considered. Perhaps these concentrations are a combination of washout from both sources. North and east of Keystone, the distributions are probably due to diffuse sources near Indiana. The temperatures on this day were around 45°F and domestic heating units would be expected to emit considerable amounts of sulfur dioxide into the quite stable surface layer. West-northwest of Keystone, the distribution is peaked at about 290° and is thought to be washout both from the Keystone plume and diffuse upwind sources. The Keystone plume was sighted between Stations C-21 and C-22, aligned with the stack height wind direction, when the collectors were being deployed. Unfortunately Station C-21 was deployed too late to receive any precipitation.

Runs 18, 19, 20 -- Although the total sampling duration spanned eight hours for this run series, the bulk of the precipitation was associated with the passage of a strong isolated thunderstorm in the morning and the frontal passage in the afternoon. Both rainfall rate and raindrop size spectra were measured at the Overlook.

The 0700 EST Pittsburgh sounding showed a deep layer of moist air which was slightly stable. Winds at the Keystone Station were initially southwest, veering to west-southwest by early afternoon and switching to west-northwest and ultimately to northwest with the frontal passage at 1555 EST.

Within ten minutes in the morning during Run 18, rainfall rates increased from about 1 mm-hr^{-1} to over 15 mm-hr^{-1} and then decreased to about 0.2 mm-hr^{-1}. The spatial variability is shown by the collector volumes in Table A.32. Although all collectors were deployed at the time of the heavy rain, those to the southeast received no rain while those to the north received their full capacity during Run 18. Run 19 collectors were exposed for about five hours between Runs 18 and 20. They sampled, to differing degrees, a final shower associated with the morning thunderstorm and a portion of the rain which preceded the front. The collectors retrieved first from Run 19 probably did not sample the prefrontal rain.

All collectors were in position for Run 20 during the major periods of precipitation associated with the frontal passage. Since they were all in position when the rain stopped, the collectors sampled the entire postfrontal rain. Variability of rain volume in the collectors was least for this run. At the Overlook, the postfrontal rainfall rate attained a value of 30 mm-hr^{-1} for a brief period.

Extremely low washout concentration of sulfur dioxide was observed in Run 18 — the lowest of the three runs. Values above the low background appeared to be randomly distributed and were probably due to local contamination. There was no evidence of washout from the Keystone plume.

Run 19 showed a marked increase in washout concentration, but it again showed no evidence of washout from the Keystone plume. Whatever variability did exist was probably due to the differences of individual collector sampling times in relation to the temporal and spatial variability of rainfall during the five hours of exposure in Run 19.

Run 20 exhibited uniformly high concentrations of washout sulfur dioxide. Though higher in concentration, the distribution was similar to Runs 9, 10, and 11, for which northwesterly winds also prevailed; though lower in concentration, the distribution also was similar to Runs 14 and 15 for for which the distributions were attributed to diffuse sources. The marked maximum shown at Station C-8 in Figure A.36, which also appears in Figure A.34 of Run 19, is assumed to be related to some local condition. Although Station C-8 was located downwind of keystone relative to the postfrontal wind direction, such was not the case during Run 19, when the wind was southwesterly.

Prefrontal wind flow was across the Pittsburgh metropolitan area, whereas postfrontal wind flow was down the corridor to the west-northwest between major cities. Flow down this same corridor in Runs 9, 10, and 11 resulted in substantial sulfur dioxide washout concentrations, but only moderate sulfate concentrations. Sulfate washout concentrations in Run 20 were about half the prefrontal concentrations. Since Run 20 includes both prefrontal and postfrontal precipitation, it is expected that the comparison of each would show even more striking differences.

The more complete sulfur dioxide concentration data were subject to an analysis to separate the prefrontal and postfrontal contributions to Run 20. This was possible due to a clear demarcation of the frontal possage time and complete postfrontal sampling. The distribution of rainfall between prefrontal and postfrontal as determined at the Overlook, was used to proportion the individual collector volumes. These volumes together with the total sulfur dioxide mass recovered in each collector were sufficient, using the method of least squares, to determine prefrontal and postfrontal sulfur dioxide concentrations. The values determined were 1.2 and 10.3 μmoles-liter for the prefrontal and postfrontal rains, respectively, and it appears that the cleaner postfrontal precipitation is much more effective in the washout of sulfur dioxide.

Run 21 -- Run 21 was a dry run to measure, under fair weather conditions, the effect on the precipitation collectors of the surface air concentration of sulfur dioxide from the Keystone stack emission. The 0700 EST Pittsburgh sounding showed a subsaturated air mass which with the moist adiabatic lapse rate would result in a thermally stable atmosphere. Rawinsonde winds were light westerly at stack height and surface winds at the Overlook veered through the period of the run from 190° to 240°. During the run, the plume was observed to cross Arc A between Stations A-7 and A-9, which would indicate a wind direction of about 250°.

Distributions on Arc A were confused by a road resurfacing operation, which apparently contaminated a number of collectors. Discounting all those beyond Station A-10, which were noted to contain dirt, peaks remain at 50° and 60° from Keystone. Peaks are noted also on Arc B at these azimuths. On both arcs extremely low concentrations appeared between these peaks, suggestive of the plume splitting which was inferred by washout sulfur dioxide distributions in Runs 2 and 6.

Run 22 -- The final run was conducted on a day with intermittent, moderate rainfall. The 1900 EST Pittsburgh sounding showed a saturated surface layer to about 4500 ft with neutral stability at stack height. The plumes were observed initially to extend from the stacks on a bearing of 120°, and a short arc was set up centered on that azimuth. Subsequently, the winds backed and the plumes were not contained.

The sampling arc did extend across approximately the southern half of the mean position of the plumes. The resulting washout concentrations were very low with a peak value of only 0.6 μmole-liter^{-1} despite the operation of both units at Keystone.

SUPPORTING STUDIES

In addition to the major field experiments just described, supporting studies were conducted to determine the degree of sulfur dioxide sorption on plume particulate and the level of sulfur dioxide in near-surface air.

The tests to measure sorption on particulate were performed using two identical electrostatic precipitators, manufactured by the Mine Safety Appliances Company, operated simultaneously under identical conditions except for the high voltage, which was turned off on one unit.

Each precipitator contained an insert of filter paper which acted as a collecting surface inside the collection tube. The inserts were impregnated with a coating solution consisting of 4 grams sodium hydroxide and 10 ml glycerine diluted to 100 ml with water. This solution provided an irreversible "sink" for any sulfur dioxide molecule incident upon the collector surface.

Since the precipitator operating at high voltage collected essentially all of the particles and the other collected essentially none, the difference between collected sulfur dioxide levels gave a measure of particulate-bound sulfur dioxide. Simultaneous operations of TCM bubblers provided a measure of ambient air concentration of sulfur dioxide.

Sulfur dioxide content of the exposed inserts was determined by extracting their contents in TCM solution using a laboratory blender, neutralizing with hydrochloric acid, and processing by means of the West and Gaeke technique.

Since the equipment was not amenable to aircraft use, operation was limited to times when the plume approached ground level. Of five attempts at measurement during the fall period, only one was successful in sampling a reasonably concentrated region of the plume. This experiment, conducted on the morning of October 29, is summarized as follows:

Average sulfur dioxide concentration in air	0.034 ppm
Amount of sulfur dioxide passed into each precipitator during sampling period	19.9 µmoles
Amount of sulfur dioxide retained by precipitator - High voltage "ON"	0.748 µmole
Amount of sulfur dioxide retained by preipitator - High voltage "Off"	0.764 µmole

These results indicate that very little sulfur dioxide existed in sorbed form in the atmosphere. The fact that the "voltage off" value exceeds the "voltage on" value arises from scatter in the experimental results.

If the reliability of the measurements is assumed to be about ± 10 percent, less than 0.4 percent of the sulfur dioxide existed in the sorbed state. This result is in accordance with previous laboratory measurements, which have indicated that the proportion of sulfur dioxide sorbed on particulate should be quite small under most circumstances.(59,60)

The sampling of near surface air to determine sulfur dioxide concentrations was performed with the Sign-X Analyzer mounted on a truck. Traverses of the arcs were made during the light rain early in Run 20 and during the no-rain condition of Run 21.

Two peaks were measured on Arc C during the rain condition traverse just prior to frontal passage. Passage of the front was recorded at 1555 by a wind shift at the Overlook from 230° to 290°. Figure 4.2 shows the air concentrations, measured in that traverse, offset for the 60° wind shift and superposed on the precipitation concentrations of sulfur dioxide which were determined. There appears to be considerable similarity between these curves. The bimodal distribution suggested here may be evidence of the plume splitting which was inferred by the washout distributions of Runs 2 and 6.

The concentrations of sulfur dioxide in air and in the collectors for Run 21, the dry run, are shown in Figure 4.3. Bimodality is shown here also. Observing the higher concentration on Arc B than on Arc A in the afternoon (p.m.) traverse, it is somewhat surprising that the dry deposition isn't significantly higher on Arc. B. However, the dry run extended over six hours from mid-morning when another traverse of Arc A (a.m.) showed much higher values than in the afternoon. When the plume is mixed to the ground in a short distance, as in the morning traverse, lower air concentration values would be expected at greater distances. Thus, the nearly equal values of dry deposition on the two arcs result from differences in mixing through the sampling period which tended to equalize exposures on the two arcs.

The mobile sampling of near-surface air concentration proved quite successful in relating this parameter to washout and dry deposition of sulfur dioxide and in documenting the plume bimodality.

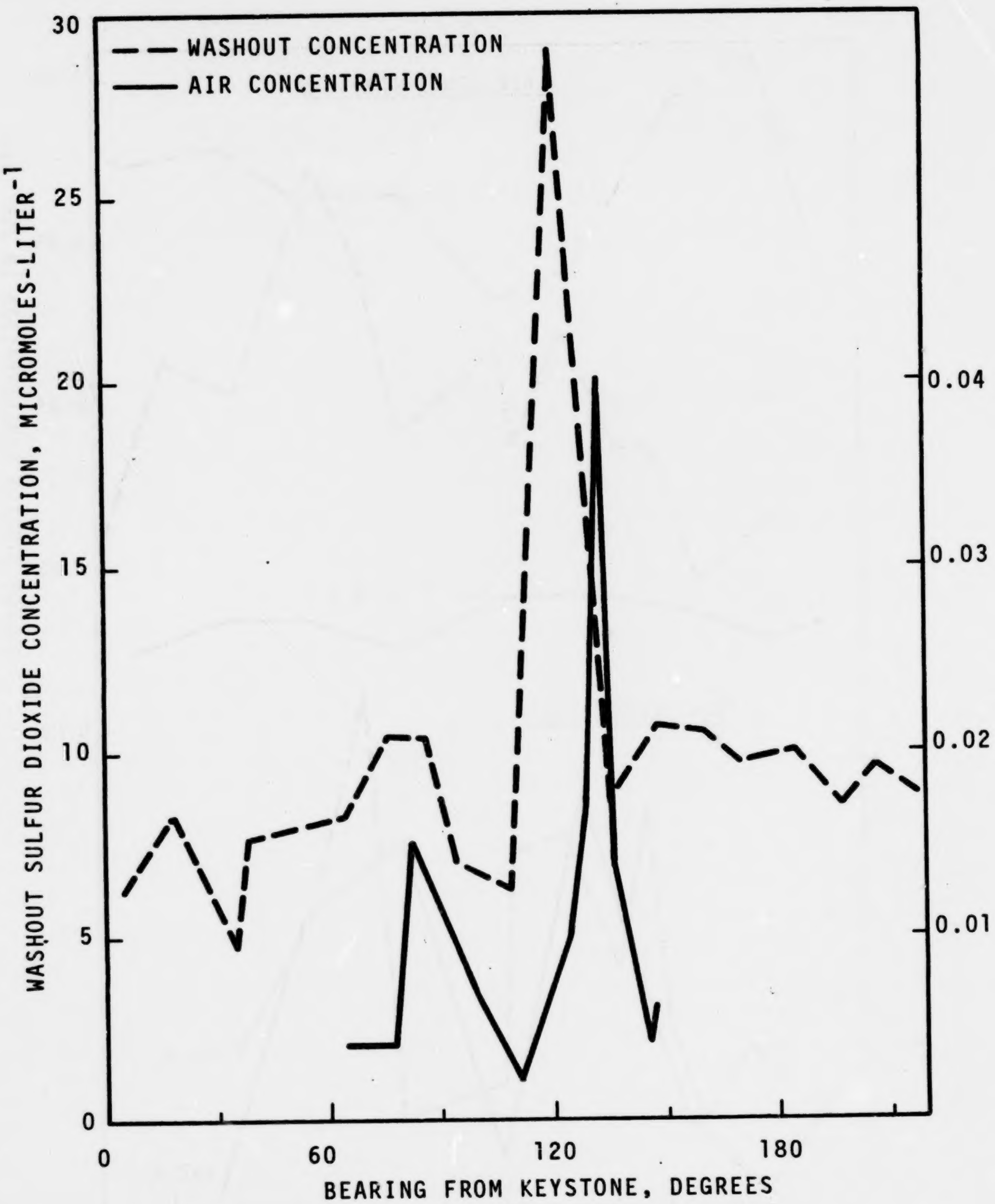

Figure 4.2 Sulfur Dioxide Concentrations in Air and in Precipitation, Run 20

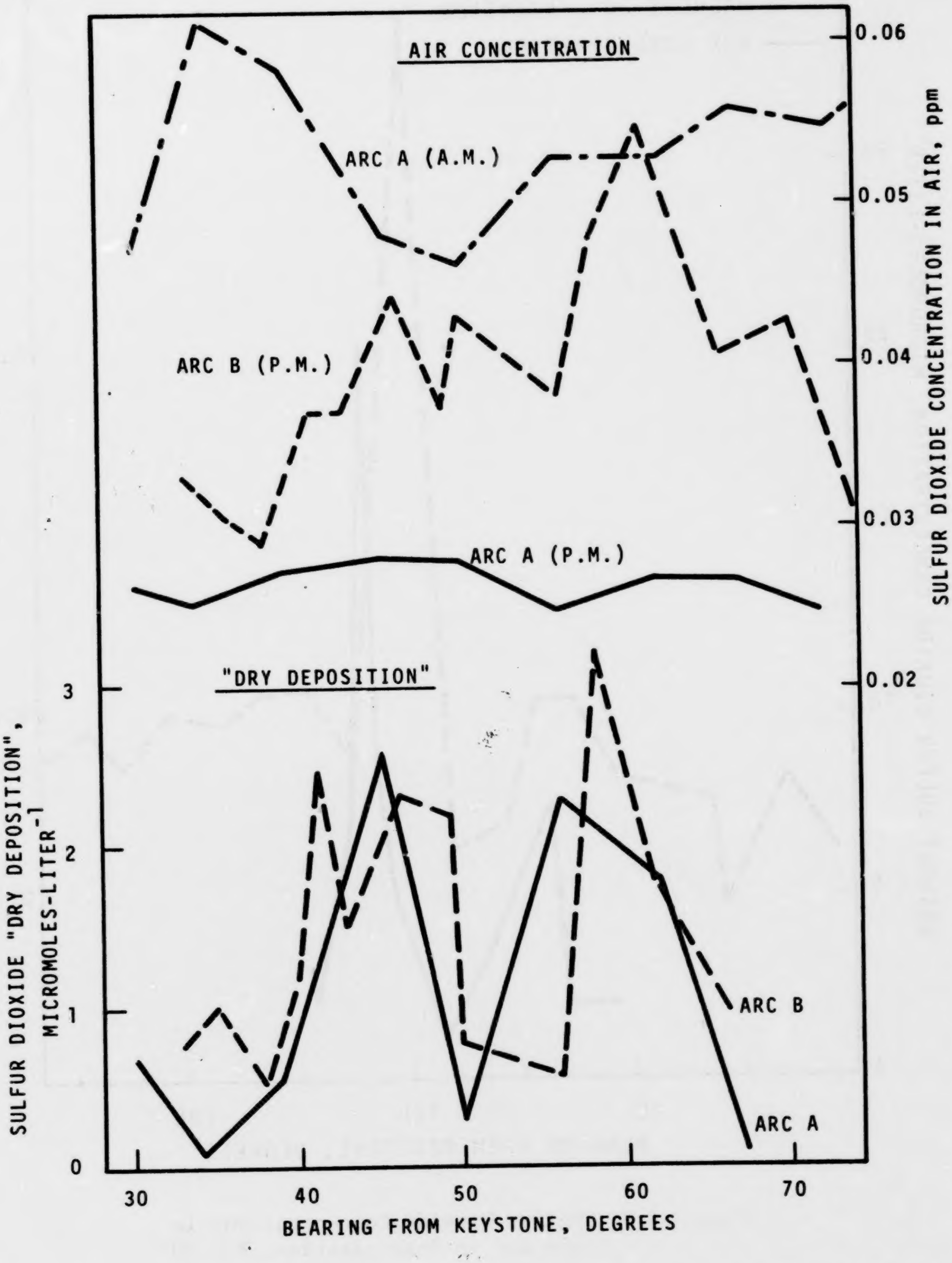

Figure 4.3 Sulfur Dioxide Air Concentration and "Dry Deposition", Run 21

CHAPTER V

DISCUSSION OF RESULTS

Chapter III presented the development of a physicochemical theory for sulfur dioxide washout which included mechanisms that were not considered in the preexisting theories of gas washout by natural precipitation. Chapter IV pointed up the extremely complex washout behavior which was observed in the field experiments. Chapter V discusses the significant field results and relates them, where feasible, to the revised theory. The theory alone provides insight into the behavior which can be expected. It might be well, therefore, to present first those considerations which have an effect on the overall results of the field experiments.

APPLICATION OF THE THEORY

Two mechanisms which are of particular importance to the washout of sulfur dioxide are the reversibility of the mass-transfer process and the solubility control exerted by the hydrogen ion concentration, or pH, of the rain. Consequences of each of these mechanisms are discussed relative to the washout of sulfur dioxide from an elevated plume.

ABSORPTION-DESORPTION OF SULFUR DIOXIDE -- The reversible nature of the mass-transfer process implies the existence of some degree of liquid-phase resistance not accounted for in the preliminary theory. Moreover, the desorption of sulfur dioxide in less concentrated regions beneath the plume should be expected to lower the net washout rates. On the basis of Figures 3.7, 3.8 and 3.9, one would expect desorption to be particularly prominent for plumes at the height of the Keystone stacks (800 ft), but much less so for plumes at lower heights. This helps to explain the much larger, irreversible, washout coefficients observed in the small scale experiments discussed in Chapter II. If fall distance beneath the concentrated region of the Keystone plume is comparable to the stack height, desorption from all but the largest raindrops should result in precipitation concentrations of sulfur dioxide in equilibrium with ground-level air concentrations. Thus, one can expect that increased plume height will result in decreased washout, which is contrary to the prediction of the preexisting theory that washout is independent of plume height. In addition, increased vertical dispersion should enhance washout for a given elevation of the plume centerline. Conditions can be postulated having the opposite effect, but they are unlikely under circumstances exemplified by the Keystone plume. The enhancement of washout by increased vertical mixing at fixed plume elevations may be viewed simply as a consequence of lessening the distance of raindrop fall "beneath" the plume, thereby providing less opportunity for desorption.

It is of interest also to examine the effect of lateral dispersion of the plume. For a fixed plume height and a constant intensity of vertical mixing, increased lateral dispersion will both dilute and broaden the plume so that it will be encountered by a greater number of drops. The significance to the total washout depends on which effect is more pronounced. Preexisting theory predicts that they are compensating. In exploring this question, it is convenient to visualize first the simplified situation of a deep plume, bordering the ground, of uniform concentration c_{Ay_1}. Rain falling through such an idealized plume will contain sulfur dioxide at a saturation value c_{Ax_1}, corresponding to c_{Ay_1}. If lateral dispersion is increased so that the plume is widened to twice its original width, the concentration will be lowered to

$$c_{Ay_2} = c_{Ay_1}/2$$

and twice as many drops will encounter the plume.

Referring to Figure 3.6, it is observed that, because of the curvature of the equilibrium line,

$$c_{Ax_2} > c_{Ax_1}/2 \quad ,$$

hence more sulfur dioxide will be removed from the wider, more dilute plume. Such reasoning can be extended to situations wherein equilibrium is not attained by the drops. Here, again because of the curvature of the equilibrium line, mass-transfer driving forces will tend to decrease with concentration in a manner such that washout is enhanced by increased lateral dispersion.

It is well to note here the differences between the effects of vertical and lateral dispersion. Increased vertical dispersion enhances washout by reducing the fall distance beneath the plume and thereby reducing the sulfur dioxide desorption. Lateral dispersion results in a lowering of drop concentration, but a net increase in washout still occurs owing to exposure to a greater number of drops.

Although plume dispersion is caused primarily by turbulent mixing, an additional mechanism which arises from desorption and fractionation of the precipitation, after plume encounter, may be important. The wide range of terminal velocities of the individual precipitation elements results in a wide range of trajectories following plume passage. This is amplified under conditions of vertical shear in the wind field. Lighter elements, in particular, are carried large distances after exposure in the plume. Consequently, the plume is broadened and deepened thereby enhancing the washout. Furthermore, washout at the ground will be related to the complex set of trajectories and exhibit a generally erratic appearance.

The above conclusions can be summarized as follows:

1. For a given plume-centerline elevation, increased mixing in any direction will enhance sulfur dioxide washout.
2. For constant conditions of mixing, increased elevation of the

plume centerline will tend to retard sulfur dioxide washout.

For situations encountered during this study, the effects of variations of plume centerline elevation with distance would be expected to be minimal compared to those arising from increases in dispersion. Hence, a general increase in washout with downwind distance should be expected — an effect that has been observed quite regularly in the field results. It is probable that this effect is much more dramatic at still greater distances than were sampled in this study. Moreover, even though washout rates observed in the first four miles downwind were rather meager, this mechanism of sulfur dioxide removal may become highly significant at greater distances from the source.

SOLUBILITY OF SULFUR DIOXIDE -- Figure 3.10 shows how the pH of water establishes the degree of sulfur dioxide solubility. Consequently, sulfur dioxide levels in rain should decrease with decreased pH of the rain. pH is determined by the dissolved, nonvolatile compounds which are taken up by the rain during its formation and fall. The pH is decreased, generally, in its passage through the plume by the washout of nonvolatile acid-forming compounds, mainly sulfates and nitrates.

The influence of the pH of the incident rain should be noted. Nonvolatile material should be washed-out irreversibly and the amount of pickup should be roughly constant for similar plume and rain morphologies. However, pH is the negative logarithm of hydrogen ion concentration, so that a given amount of acid-forming material will be more significant in reducing the pH if the incoming rain has a high pH.

The significance of the rain pH is that low values will limit the solubility of sulfur dioxide thereby reducing its absorption or enhancing its desorption. The greatest washout should occur from a pure sulfur dioxide plume in a clean atmosphere and far less from a typical power plant plume in an already polluted atmosphere.

SULFUR DIOXIDE WASHOUT

There were few, if any, runs in which the sulfur dioxide distributions were sufficiently well-defined for the calculation of washout coefficients. Given a single source of known output and containment of its plume, this is a straight-forward calculation under the assumption of an irreversible, first order process. However, none of these requirements were met in this study. Background values were often high and variable presumably because of a number of large and small sulfur dioxide sources in the area. Consequently, separation of the component of washout from the Keystone Station plume was generally not possible.

In those cases, where sulfur dioxide washout could be related to other sources on the basis of the observed wind field, containment was incomplete and the sampler configuration was not suitable for the calculations of the washout coefficient from those sources, either. However, where components of the distribution were identifiable with sources, either Keystone or others, the observed peak values of concentration were taken for analysis.

These values together with the precipitation volume collected and the duration of exposure of the collector were sufficient to define the washout flux of sulfur dioxide and the concurrent precipitation rate. A summary of these data is presented in Table 5.1 together with identification of the probable sources of the concentration maximums. Specific sources are the Keystone and Homer City generating stations and the Lucerne coke ovens. A general source identified as "Area" is noted for those run distributions which were sufficiently homogeneous to indicate the entire grid was blanketed from diffuse sources at a moderate distance.

Figure 5.1(a-c) show the washout flux as a function of precipitation rate for the various sources. The two identified sources, Homer City and Lucerne, are plotted together. The unidentified area sources and Keystone are each plotted separately. The relationship between the flux and the

TABLE 5.1

PEAK WASHOUT CONCENTRATIONS AND FLUXES

Run No.	Station No.	Apparent Source	Conc. $(\frac{\mu mole}{liter})$	Volume (ml)	Exposure Duration (min)	SO_2 Flux $(\frac{\mu mole}{m^2\text{-}hr})$	Precipitation Rate $(\frac{mm}{hr})$
1	A13	Area	6.5	74	56	5.7	0.88
1	B12	Area	9.8	66	55	7.9	0.80
2	A64	Homer City	8.8	52	122	2.5	0.28
2	B89	Homer City	16.7	32	126	2.8	0.17
3	A51	Homer City	9.0	16	117	0.8	0.09
3	B69	Homer City	6.5	20	114	0.8	0.12
4	A60	Homer City	12.3	122	68	14.7	1.20
4	B63	Homer City	10.4	89	66	9.4	0.90
5	A57	Homer City	10.8	91	107	6.1	0.57
5	B68	Homer City	8.8	77	98	4.7	0.52
6	A22	Keystone	1.7	83	139	0.7	0.40
6	B42	Keystone	4.4	43	136	0.9	0.21
7	A2	Homer City	12.8	134	86	13.3	1.04
7	B90	Homer City	7.2	149	98	7.3	1.01
8	A2	Homer City	9.5	72	73	6.2	0.66
8	B58	Homer City	12.1	27	51	5.0	0.35
9	A50	Area	13.2	72	81	7.8	0.39
9	B47	Area	11.8	90	93	7.6	0.65
10	A68	Area	8.8	92	94	5.8	0.65
10	B30	Area	9.8	106	96	7.2	0.74
11	A38	Area	7.8	65	115	3.0	0.38
11	B47	Area	11.1	84	129	4.8	0.43
12	B60	Keystone	3.5	24	139	0.4	0.12
12	B46	Lucerne	3.2	25	164	0.3	0.10
14	B64	Keystone	5.0	245	107	7.6	1.53
14	B64	Area	16.0	245	107	24.4	1.53
15	B64	Keystone	2.0	225	123	2.4	1.22
15	B64	Area	14.0	225	123	17.1	1.22
16	C22	Keystone	13.1	28	25	9.9	0.75
16	C14	Lucerne	27.8	20	23	16.2	0.58
18	C29	Area	1.6	262	76	3.7	2.30
19	C11	Area	8.7	50	47	6.2	0.71
20	C18	Area	11.0	212	72	21.6	1.96
22	B24	Keystone	0.6	118	215	2.2	0.36

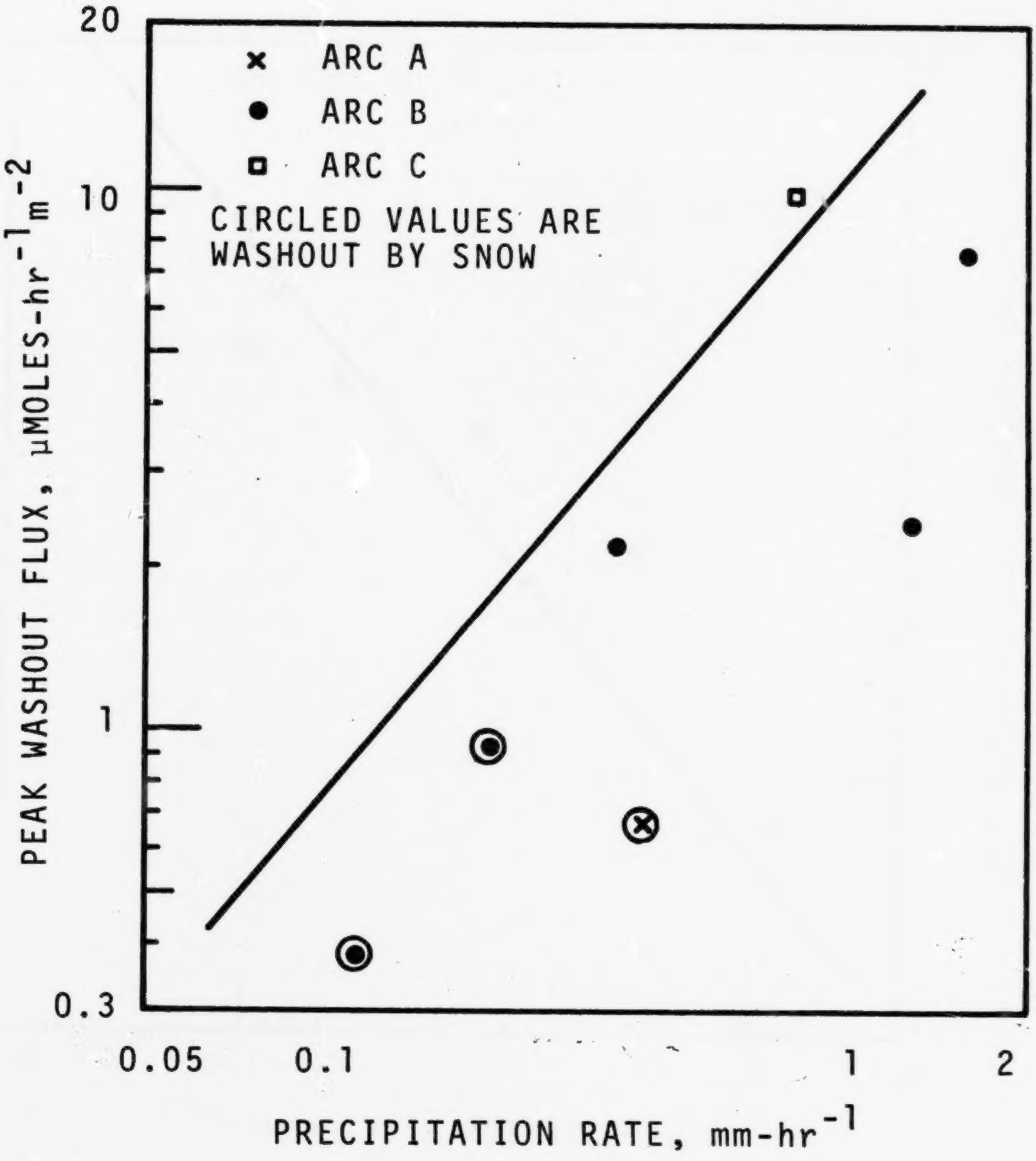

Figure 5.1(a) Peak Sulfur Dioxide Washout Flux From Keystone Plume

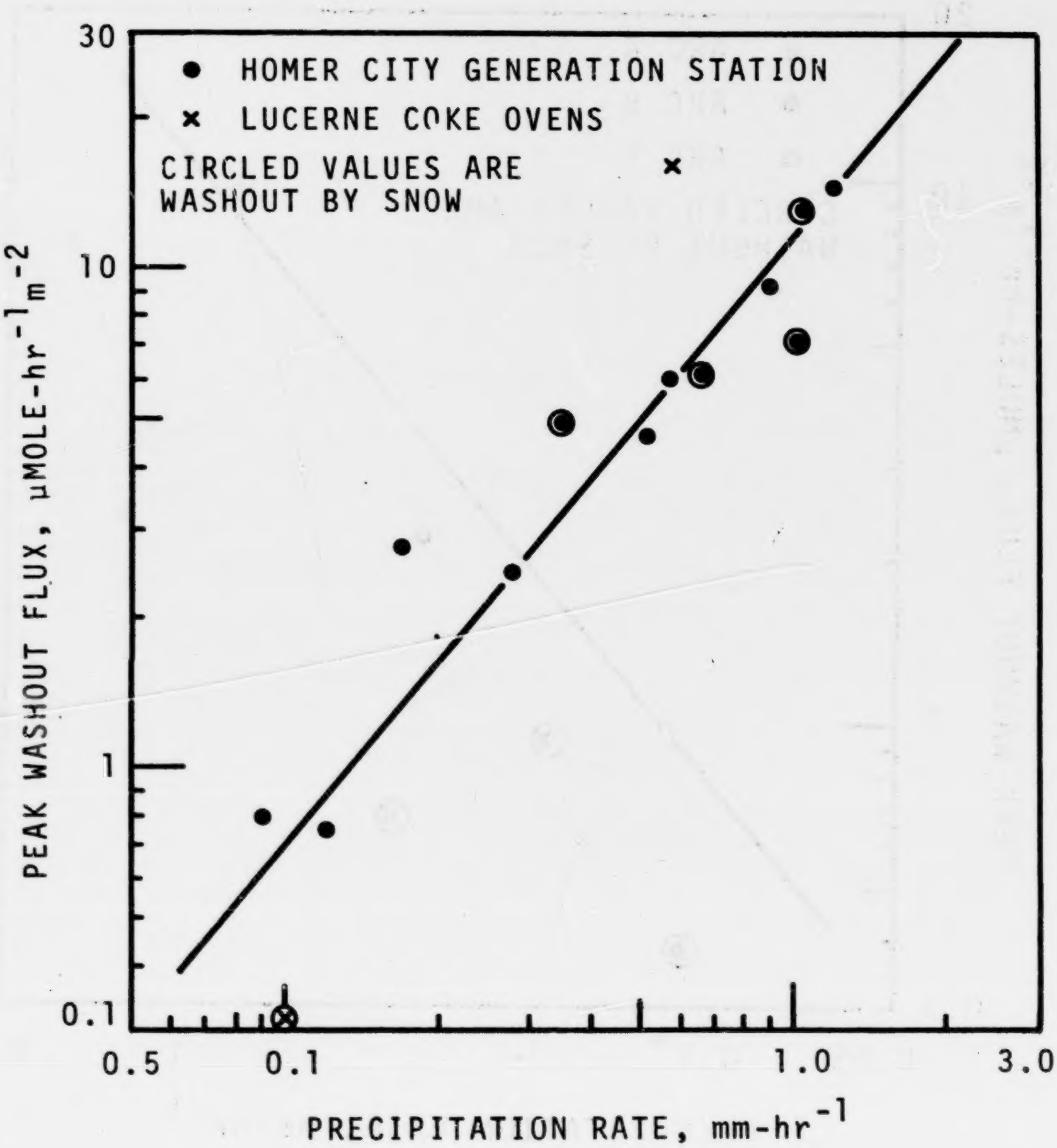

Figure 5.1(b) Peak Sulfur Dioxide Washout Flux From Other Local Sources

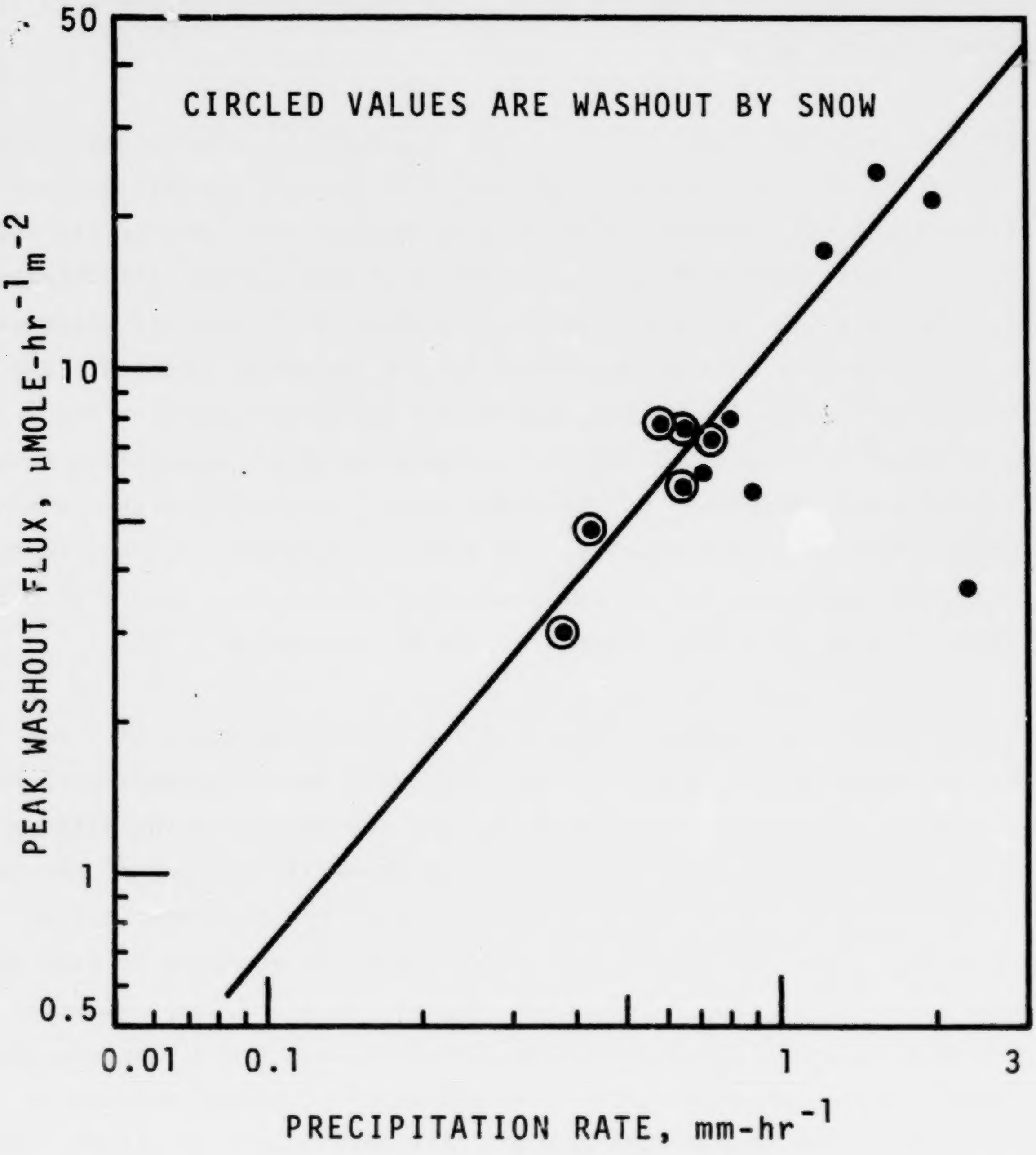

Figure 5.1(c) Peak Sulfur Dioxide Washout Flux From Unidentified Sources

precipitation rate is shown best by the Homer City washout contributions, Figure 5.1(b), which are distributed over a wide range of precipitation rates. The slope of the line, which was drawn as a visual best fit, is measured as 1.23. This slope is seen to be compatible with the data from the other sources as well.

The earlier works by Chamberlain(52) and Engelmann(53) show slopes less than unity for the theoretical relationship of washout coefficient and precipitation rate. Various raindrop size spectra were used in the calculation of their curves which were based on a first order, irreversible model. The selected raindrop size spectra shown in Figure 5.2 which were taken during washout runs at Keystone, are not markedly different from spectra that they employed. The significant difference between the observed slope of Figure 5.1 and the slopes defined by preexisting theory testifies to the inadequacy of the first order, irreversible approximation for the washout of sulfur dioxide. As shown in Chapter III, many factors which are not accounted for in the simplified preexisting theory affect the gain and loss of sulfur dioxide by the precipitation.

The curve through the washout flux data for sources at Homer City and Lucerne is shown on the other figures to provide ready comparison of the three sets of data. Although the curve fits the data from the diffuse sources of Figure 5.1(c), it is seen to lie above all but one of the data points in Figure 5.1(a) which were attributed to the Keystone Station contribution. This one point which lies within the grouping of data for the other sources is from a collector position on Arc C, approximately 4 miles from Keystone. The lower values for Arc A and Arc B samplers are attributed to the low near-surface concentration of sulfur dioxide at short distance from an elevated source. All data points in Figure 5.1(b) represent fluxes 10-15 miles from their sources where surface concentrations can be assumed to have been increased by the downward diffusing plume.

No apparent difference between washout of sulfur dioxide by rain and by

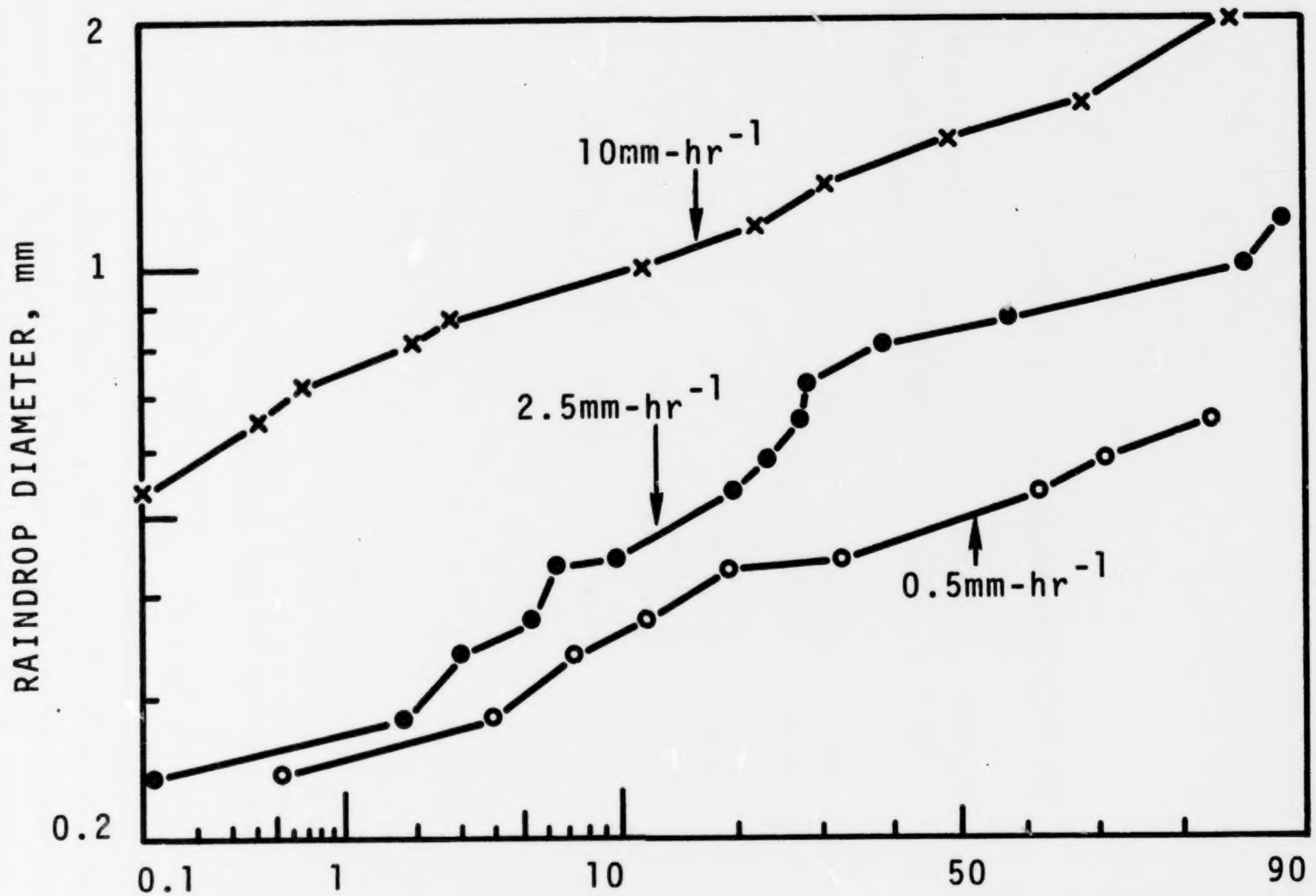

Figure 5.2 Selected Raindrop Spectra, Indiana County, Pennsylvania

snow is seen in Figures 5.1(a-c). However, when the values for snow are normalized to unit precipitation rate using the experimentally determined slope, Runs 6 and 12 demonstrate appreciably lower values as is shown in Table 5.2.

TABLE 5.2

SULFUR DIOXIDE WASHOUT FLUX IN SNOWFALL[a]

Date	Run No.	Station No.	Apparent Source	Temperature (°F)	Sulfur Dioxide Flux (μmole m^{-2}-hr^{-1})
2-03-70	6	A-22	Keystone	15-20	2.1
	6	B-42	Keystone		6.5
2-09-70	7	A-2	Homer City	35	12.5
	7	B-90	Homer City		7.2
	8	A-2	Homer City		10.2
	8	B-58	Homer City		17.5
2-10-70	9	A-50	Area	33	14.9
	9	B-47	Area		13.0
	10	A-68	Area		9.9
	10	B-30	Area		10.3
	11	A-38	Area		9.6
	11	B-47	Area		13.1
2-14-70	12	B-60	Keystone	20	5.0
	12	B-46	Lucerne		5.5

(a) Flux values normalized to unit precipitation rate.

Several explanations are possible for this observed difference. Certainly a factor on Arc A of Run 6 is the aforementioned necessity for the plume growth to be sufficient to raise the near-surface sulfur dioxide concentration. The large difference between Arc A and Arc B concentrations indicates that the plume had not reached the ground in sufficient concentrations on Arc A. An inversion was present to well above the stack in this run and such behavior would be expected. During Run 12, however, neutral stability was indicated by the Pittsburgh rawinsonde and the mixing should have been adequate. The washout flux from the Lucerne coke ovens, a surface source, is comparable to that from the Keystone Station in Run 12.

It should be noted that Runs 6 and 12 both occurred on days with the temperature well below freezing, whereas, the other snow runs were conducted with surface temperatures above freezing. Snow characteristics consequently were different, and this is shown by Figure 5.4(a-d), photographs of the snow on each of the snow run days. Figures 5.4(a) and (d), which were taken during Runs 6 and 12, respectively, show the dry, crystalline character of the snow during these runs. Figures 5.4(b) and (c) show, as clearly, the wet amorphous nature of the snow during Runs 7 and 9. The light shading across Figure 5.4(b), in fact, is melt water or rain which also fell.

Whereas sulfur dioxide washout by wet snow, falling in near-freezing conditons, is comparable, apparently, to washout by rain, it is suggested that dry snow is less effective in the removal. Whether the effect is solely one of temperature cannot be determined from the data which are grouped closely both above and below freezing. It is possible that higher washout is associated with a water film on the snow. Further investigation of this effect is necessary.

Some comparison of the observed fluxes with those predicted by the preexisting model are possible recongnizing that Equation 2.4 can be written as,

$$\Sigma m_i/NAt = \Lambda R/(N\Delta Y\bar{u}) \qquad (5.1)$$

where R is the rate of emission of sulfur dioxide, t is the sampling time

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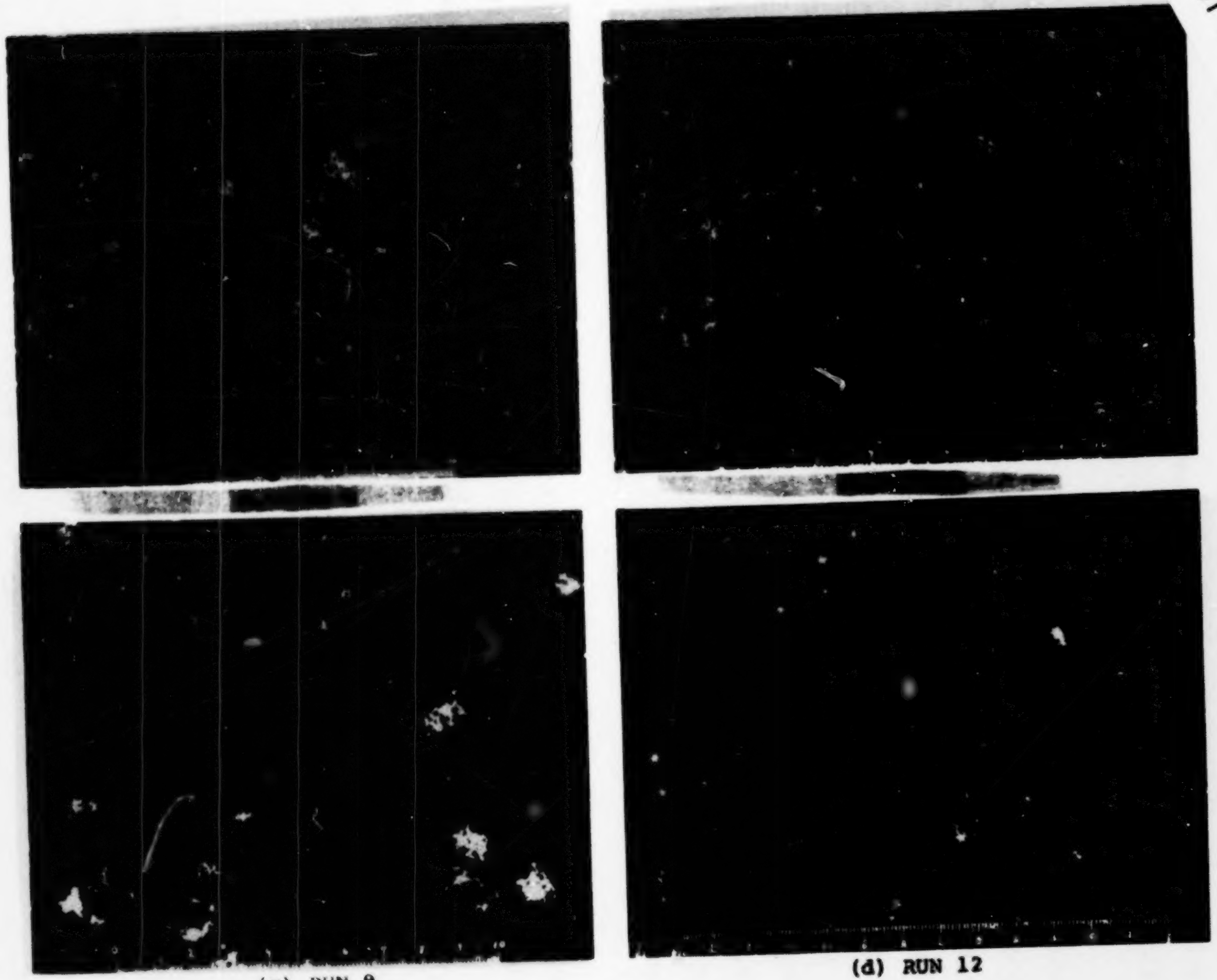

(c) RUN 9

(d) RUN 12

Figure 5.3 Snowflake Character

and N is the number of samplers which receive washout from the emitter. The other symbols were defined earlier. The term on the left is the average flux. Using the washout coefficient of 10^{-4} sec^{-1} given by Chamberlain(52) as appropriate for a precipitation rate of 1 $mm\text{-}hr^{-1}$ and assuming an emission rate of 3×10^3 $gm\text{-}sec^{-1}$, a wind speed of 10 meters sec^{-1} and a plume width of 1500 meters on Arc B, a flux of approximately 1000 μmoles $(m^2hr)^{-1}$ is calculated. Observed values were seen to be less by factors of 50 to 100.

As noted earlier, Run 21 was conducted to ascertain the direct influence of sulfur dioxide concentrations on the collectors — a measure of the dry deposition. If it is assumed that the peaks observed in Figure 4.3 were due to the Keystone plume alone, except for the observed background of 0.1 $\mu mole\text{-}liter^{-1}$, the peak value represents a mass of 0.016 μmole delivered to the collector in four hours. At the deposition rate of 0.004 $\mu mole\text{-}hour^{-1}$, few runs would be influenced by the effect. Exceptions are collectors which were exposed for long periods in light, intermittent precipitation. It should be noted, however, that the mobile sulfur dioxide analyzer, which was operated at the station receiving the peak deposition, showed air concentrations between 0.05 and 0.1 ppm, values which were much higher than detected during washout runs.

Figure 5.4 presents the sulfur dioxide concentration data of Table 5.1 plotted against the total time of collector exposure — not the precipitation periods only as tabulated there. The peak value of 27.8 $\mu mole\text{-}liter^{-1}$ is the one most likely to have been increased by dry deposition of sulfur dioxide. This collector was exposed for 207 minutes and collected 20 ml of precipitation. Using the deposition rate determined from Run 21, the concentration resulting from dry deposition is determined to be 0.7 $\mu mole\text{-}liter^{-1}$, which is only 2.5 percent of the observed concentration. Consequently, dry deposition is not considered a serious problem.

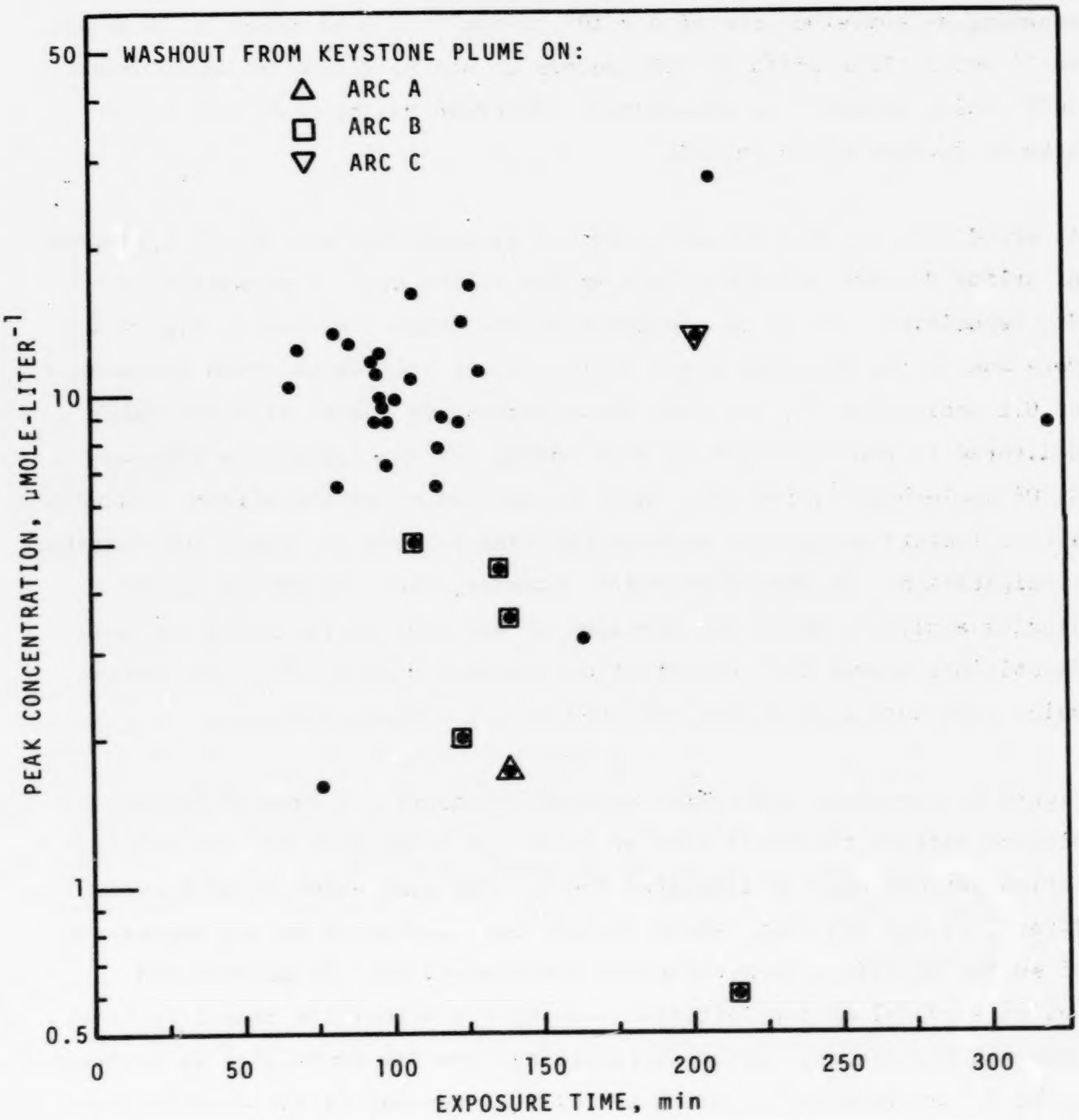

Figure 5.4 Comparison of Peak Sulfur Dioxide Washout Concentration and Collector Exposure Time

The grouping of values near 10 μmole-liter^{-1} in Figure 5.4 emphasizes the dependence of washout sulfur dioxide concentration on surface air concentration and precipitation acidity as discussed previously. This value is in equilibrium with air concentrations of 0.01 to 0.03 ppm when the precipitation has a pH value between 4.0 and 4.5. These ranges of air concentration and pH were observed.

A further observation emphasized in Figure 5.4 is the necessity for sampling the Keystone plume at greater distances where its proximity to the ground results in greater washout. Only the Arc C measurement of the Keystone plume shows a washout concentration comparable to those from more distant sources of presumably lower emission rates.

It is useful to compare surface concentrations resulting from various sources in light of the importance of the sulfur dioxide concentration near the ground in washout. The method of Smith and Singer(61) was used for this comparison. A neutral atmosphere bounded by stability Classes B_1 and C and a wind speed of 5 meters-sec^{-1} at all levels were assumed. For the stack release, a plume rise of 600 ft was determined using the method suggested by Carson and Moses.(62) The heat emission rate was taken as 2.5×10^4 kilocalories/sec, an approximate value appropriate for the Keystone or Homer City Stations. The results are given in Table 5.3 in terms of parts per million of sulfur dioxide per ton released per hour. Surface concentrations can be calculated if the source term is defined. This can be done readily for the generating stations, but the output from the coke ovens is unknown. The similarities in observed washout values and in calculated values for air concentration for Homer City and Lucerne suggests that their emission rates are comparable.

The extremely low value at Arc A resulting from the Keystone plume under the more stable Class C is due to the low diffusion rate which prevents mixing of the plume to the ground at that distance. Other values in the table yield concentrations of 0.01 to 0.2 ppm for typical emission rates

TABLE 5.3

COMPARISONS OF SURFACE CONCENTRATIONS[(a)] UNDER NEUTRAL STABILITY CONDITIONS

	Stability Class	
Condition[(b)]	B_1	C
1	3.47×10^{-3}	2.19×10^{-14}
2	1.82×10^{-2}	9.91×10^{-4}
3	9.81×10^{-3}	1.48×10^{-3}
4	1.31×10^{-3}	8.60×10^{-3}
5	1.34×10^{-3}	1.13×10^{-2}

(a) Values are in units of ppm-hr-ton^{-1}. The product of these values and the source strength in tons-hr^{-1} is the surface concentration in ppm.

(b) Condition 1. Concentration at Arc A from Keystone source (4,000 ft)
Condition 2. Concentration at Arc B from Keystone source (12,000 ft)
Condition 3. Concentration at Arc C from Keystone source (22,000 ft)
Condition 4. Concentration at Arc B from Homer City source (80,000 ft)
Condition 5. Concentration at Arc B from Lucerne source (80,000 ft, ground release)

of 10-20 tons per hour from the generating stations. These concentrations are appropriate to retain sulfur dioxide concentrations of 1 to 50 μmoles-liter^{-1} in the precipitation under equilibrium conditions.

A prominent feature of the distributions of washout sulfur dioxide concentration is the absence of positive correlation with the Keytone plume. This, apparently, is a consequence of the shallowness of the plume at short distances from the source which permits the least time for sulfur dioxide sorption and the greatest time for its desorption. An additional feature, less easy to reconcile, is the negative correlation of washout beneath the plume. This was observed in Runs 4 through 11. Except for Run 6, which is discussed later, these "troughs" occurred in a homogeneous distribution of sulfur dioxide washout from other sources. It appears, therefore, that the washout of sulfur dioxide from these sources was inhibited in some way by the Keystone Station, or that the sulfur dioxide was converted to sulfate.

[illegible]LFATE WASHOUT

Sulfate washout values were examined for the runs which displayed decreases in sulfur dioxide washout beneath the expected, plume position. Peaks were noted at or adjacent to all stations which had minimum sulfur dioxide washout values. Sub-plume and background washout flux values of sulfate and sulfur dioxide are shown in Table 5.4. The value from a single station was tabulated if the maximum sulfate and minimum sulfur dioxide fluxes occurred at the same collector station. If they occurred at adjacent stations, the average value for the two stations was used. In all cases the background value was determined by the average of values at the three stations on each side of the central station or pair of stations.

The sulfate washout flux attributed to the plume is the difference between the sub-plume and the background fluxes. It is uncertain that the plume sulfate washout flux is derived totally from the stack emission. It is possible that background sulfate washout is enhanced by exposure to the plume. The additional humidity within the plume may, for example, condense on the sulfate. More effective washout would result for the droplet than for the submicron sulfate particle. However, the sub-plume washout flux diminished by the background washout flux is referred to here as the plume washout flux.

TABLE 5.4

FLUXES OF WASHOUT SULFATE AND SULFUR DIOXIDE

Run No.	Station No.	Precipitation Rate	Sulfur Dioxide Flux		Sulfate Flux	
			Background	Sub-Plume	Background	Sub-Plume
		($mm\text{-}hr^{-1}$)	($\mu mole\ m^{-2}\ hr^{-1}$)		($mg\ m^{-2}\ hr^{-1}$)	
			RAIN			
4	A-55	1.16	7.10	2.36	2.79	4.24
4	B-79, B-80	0.79	5.51	1.99	2.49	3.16
5	A-53, A-54	0.54	4.12	1.03	1.60	2.30
5	B-78	0.42	1.12	0.10	1.20	1.74
			SNOW			
7	B-52	1.38	8.02	5.93	6.30	25.10
7	B-72	1.18	2.35	1.26	5.52	12.50
9	B-22	0.77	5.64	2.66	2.94	6.18
11	A-18	0.34	1.60	1.01	1.73	2.64
11	B-24	0.34	1.79	1.24	1.08	1.46

Washout fluxes for both the background sulfate and the plume sulfate are shown in Figure 5.5. The background values in both rain and snow and the plume values in rain are observed to be linearly related to the precipitation rate. This relationship has been observed previously for aerosol washout.(5,63) The washout of sulfate from the plume by snow, however, appears to be dependent on the square of precipitation rate. Unquestionably, this relationship stems from an interaction between the snow and some special property of the plume. This property may be the humidity which provides high supersaturation relative to the snow.

The question of sulfate origin cannot be answered conclusively, but it is possible to estimate the extent of sulfur dioxide oxidation required to explain the observed sulfate flux. Equation 5.1 can be rewritten as

$$R' = FN\Delta Y\bar{u}/\Lambda \tag{5.2}$$

where, R' is the sulfur, as sulfate, emission rate and F is the mean sulfur, as sulfate, washout flux over the plume width, $N\Delta Y$. Calculations were made using run data including flux values from Table 5.4 which were normalized to unit precipitation rate with appropriate slopes for rain and snow. The washout coefficient value of $5 \times 10^{-6} \text{sec}^{-1}$, which is appropriate for submicron particle washout at unit precipitation rate, was assumed.(5) These results were then divided by the Keystone Station sulfur emission rate during the runs to obtain the percent oxidation required.

Figure 5.6 compares the calculated oxidation as a function of travel time to the collector with oxidation data presented by Gartrell, et al.(64) who measured oxidation at various distances with an instrumented aircraft. Their finding, that catalytic oxidation either occurs at a high rate, 1-2 percent per minute, or does not occur, was borne out by Baldwin, et al.(65) and Arin, et al.(66) who found essentially no change in sulfur dioxide beyond one kilometer. The overall agreement of calculated

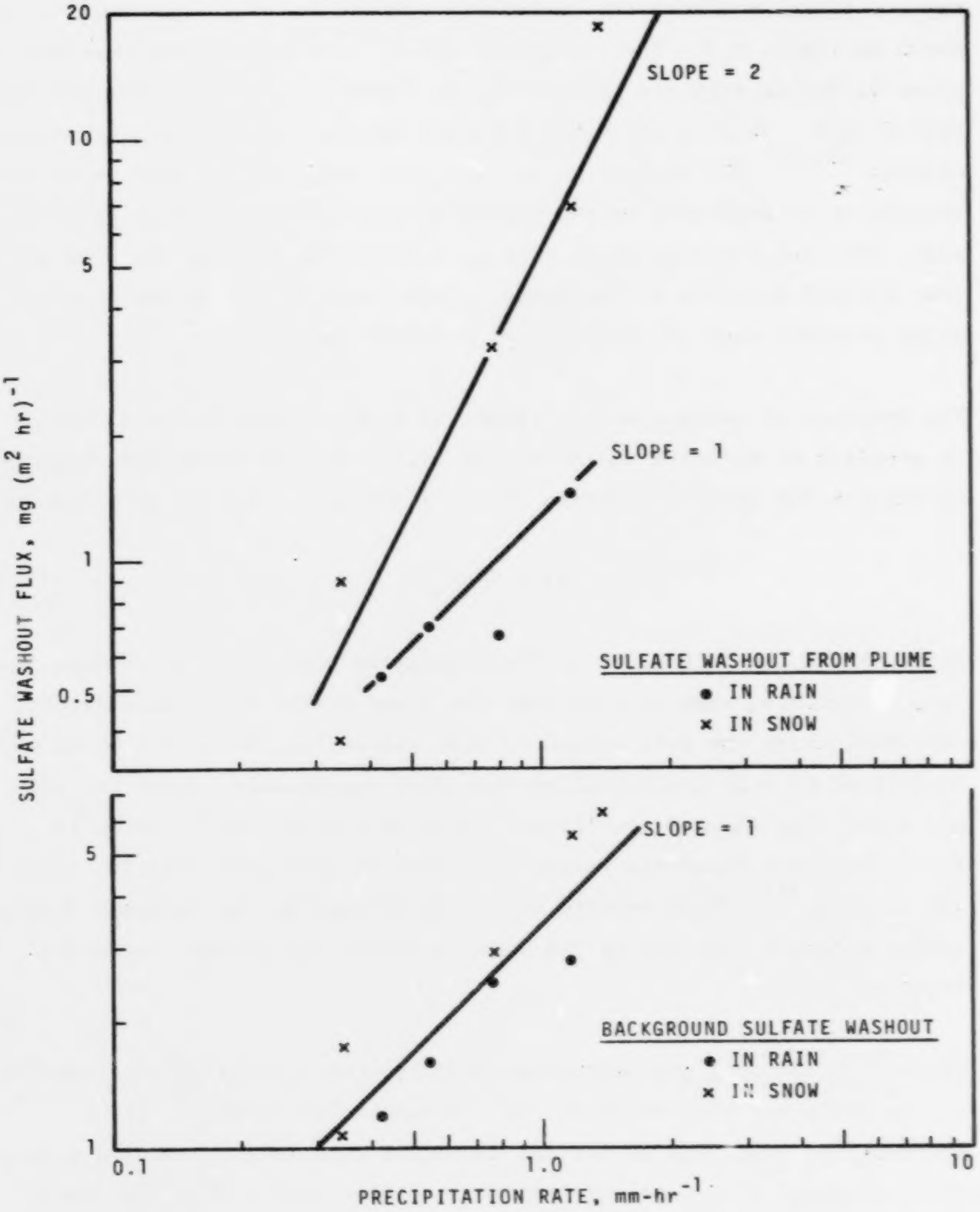

Figure 5.5 Sulfate Washout Fluxes

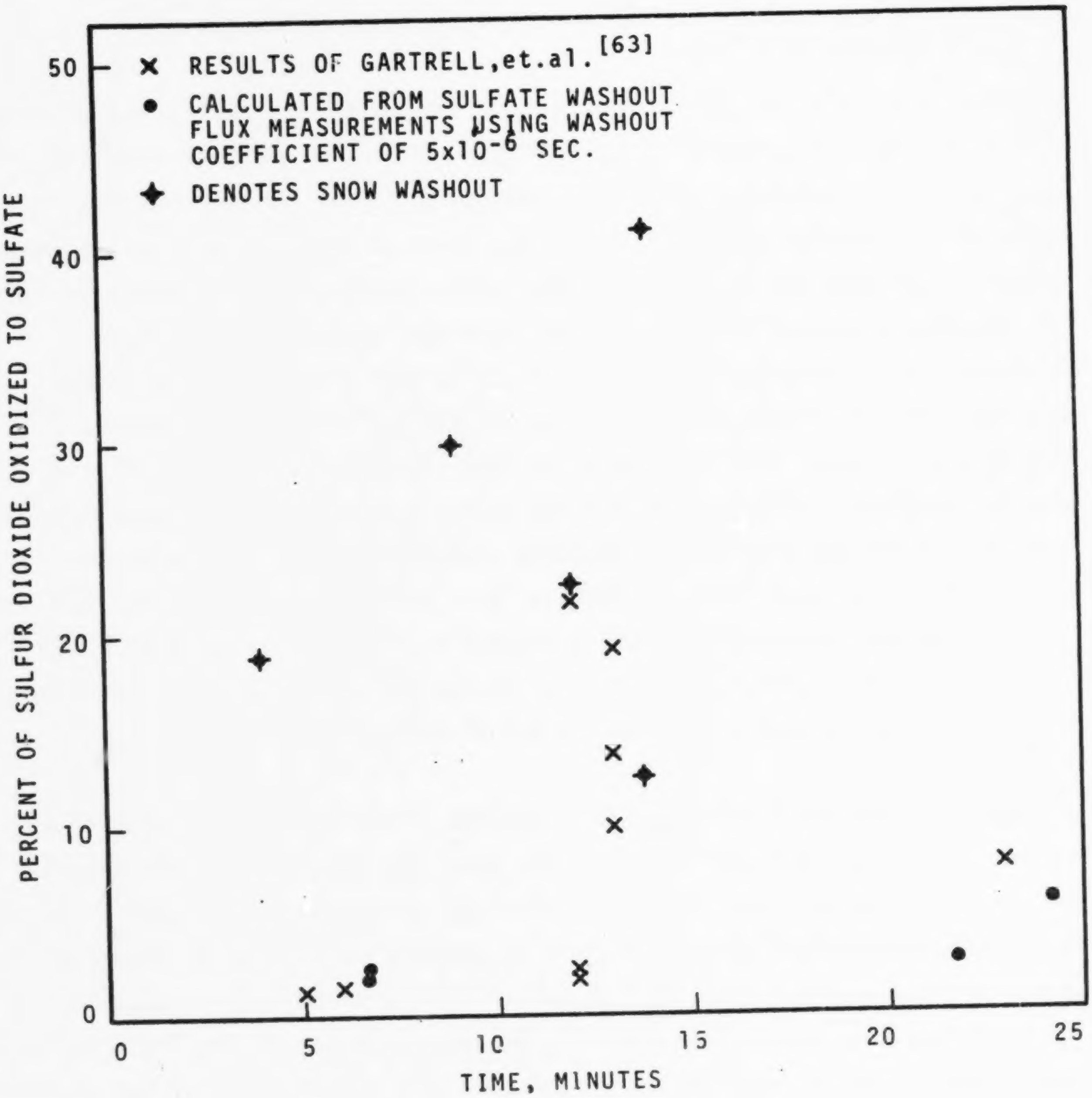

Figure 5.6 Rate of Sulfur Dioxide Oxidation

oxidation with the results of Gartrell is striking. The generally higher calculated values which are derived from the snow washout flux data may be due either to enhanced oxidation or to more efficient washout. The use of the submicron washout coefficient would be inappropriate if condensation on the sulfate nuclei resulted in substantial growth.

Assuming that only one to two percent of the sulfur is emitted as sulfate,(64) it appears probable that the observed sub-plume sulfate resulted from catalytic oxidation of sulfur dioxide and that its washout was enhanced by condensation of plume water vapor on the sulfate nuclei when temperatures were near freezing. The fact that maximum decreases in sulfur dioxide occurred during rain, and maximum increases in sulfate occurred during snowfall indicates that the two are not well related. However, the decreased sulfur dioxide in the sub-plume collectors is likely a consequence of the low pH of the precipitation caused by the sulfate acidity. More sulfur dioxide might be retained in a snowflake than in a raindrop because the sulfate particle sorbed on the former would exhibit a local effect, whereas in a raindrop, it would mix and totally inhibit the sulfur dioxide retention. Higher background sulfate washout flux in snowfall probably is due to the higher sulfate concentration in the air during winter as reported by Junge.(67)

It appears from the foregoing that, whereas the washout of sulfur dioxide from the Keystone Station may be light near the source, sulfate washout may be appreciable. For example, Table 5.2 shows that the washout flux of sulfur dioxide is on the order of 10 μmole$(m^2hr)^{-1}$, while Figure 5.5 shows sulfate washout flux of 5 mg$(m^2hr)^{-1}$ for a comparable precipitation rate. Comparing the sulfur removal, the sulfate washout accounts for about five times as much as the sulfur dioxide washout. As noted earlier, the sulfur dioxide washout should increase with distance, whereas the data of Table 5.4 suggest that sulfate washout will decrease with distance.

CHAPTER VI

CONCLUSIONS

This investigation of sulfur dioxide washout from plumes emitted by tall stacks has provided significant new information on the washout of gaseous effluent. The theoretical development of Chapter III has provided insight into the physicochemical influences which are important in sulfur dioxide washout. It has shown that liquid phase phenomena can substantially alter the washout effectiveness of rain. Rates of sulfur dioxide sorption and desorption are dependent on the size and chemical composition of the raindrop as well as on the instantaneous concentration of sulfur dioxide in the air. Highly acid (low pH) rainwater has a markedly reduced affinity for sulfur dioxide, which is highly soluble in a neutral solution. Large drops rapidly reach their equilibrium concentration only if vigorous mixing is present within the drop, whereas small drops attain equilibrium rapidly by molecular diffusion alone. In the absence of an irreversible chemical reaction to retain the sorbed sulfur dioxide, it will desorb in a region of lower sulfur dioxide concentration. Thus, drops falling below the plume will continually desorb their sulfur dioxide content. The smallest drops collected will be essentially in equilibrium with the surface air, while larger drops will retain some "memory" of the plume.

It follows, therefore, that washout from a plume is highly dependent on the geometry of the plume and the characteristics of the rain. Clean rainwater falling through a low elevation, concentrated plume will exhibit concentrated washout, while acid rainwater falling through either a low or a high elevation, concentrated plume will fail to record its presence. However, if the plume from a high elevation source is spread in the vertical so as to approach the ground, clean rainwater will remove substantial sulfur dioxide from it as well, since a large change in air concentration will result in a smaller change in equilibrium concentration. This fact also results in greater depletion of the airborne sulfur dioxide in a plume which is widely dispersed laterally since the areal coverage over-compensates for the reduced concentration.

It should be emphasized that appreciable sulfur dioxide cannot be removed unless surface air concentrations are substantial and the precipitation acidity is low. Consequently, the maximum washout of sulfur dioxide emitted from a tall stack is likely to occur at the distance of maximum surface air concentration when background air pollutants do not lower the precipitation pH. Furthermore, since other pollutants from the stack emission tend to decrease the precipitation pH, they also inhibit sulfur dioxide washout. It has been concluded from the theoretical analyses that direct gas absorption is the most important washout mechanism. Washout of aerosols containing sorbed sulfur dioxide is of negligible consequence in this respect. Precipitation as snow has not been considered in the theoretical development, but from the experimental results, similarities in the washout of sulfur dioxide are evident.

Analysis of the experimentally determined fluxes of sulfur dioxide has shown a relationship to precipitation rate which is inconsistent with the first order, irreversible assumption used in the preexisting theory of gas washout. Whereas, the theory showed washout increasing at a lower rate with high precipitation rates, the experimental data show disproportionately more effective washout at higher precipitation rates. This inference of higher washout efficiencies for larger drops is in agreement with the theoretical development of Chapter III. There was no apparent stratification of the data according to the precipitation type — both rain and snow washout was equivalent for a given precipitation rate, as noted above. Washout flux was estimated to be proportional to the 1.23 power of precipitation rate. Closer scrutiny of the snowfall data did indicate lower washout flux values during dry snow runs, but too many variables are present to draw conclusions from those sparse data.

Washout flux values were consistently less than predicted from preexisting theory and lowest values were associated with emissions from the Keystone Station, except in one instance. On arc C, flux values comparable with other sources were observed. Although this arc is 4 miles from the Keystone Station and suitably located to receive substantial air concentrations of sulfur dioxide under some conditions, it is suspected that a portion of this flux value can be attributed to an upwind source. Fluxes from upwind sources — some identified and some not — were clustered about a value of 10 μmoles$(m^2\text{-hr})^{-1}$ normalized to a precipitation rate of 1 mm hr^{-1}. For a pH value between 4.0 and 4.5 this value is in equilibrium with air concentrations of 0.01 to 0.03 ppm. These ranges of air concentration and pH were observed generally, though higher concentrations were observed and also computed using atmospheric diffusion techniques. Maximum observed fluxes were below 30 μmoles$(m^2\text{-hr})^{-1}$. Fluxes up to two orders-of-magnitude greater are predicted by the preexisting theory.

An interesting feature of several runs was increased sulfate and decreased sulfur dioxide washout fluxes, compared with background values, in a region beneath the expected trajectory of the Keystone plume. The decrease in sulfur dioxide flux is not sufficient to account for the increase in sulfate flux, nor are they quantitatively related in any simple way. Maximum decrease in sulfur dioxide flux occurred in rain, while maximum increase in sulfate flux beneath the plume occurred in snowfall. Decreased pH from sulfate sorption apparently caused the sulfur dioxide deficiency. It is uncertain that all of the sulfate was derived from the Keystone Station, although calculations of the required sulfur dioxide oxidation in the plume were in general agreement with oxidation rates observed by others. Highest values of sulfate which occurred beneath the plume during snowfall are attributed to rapid oxidation of the sulfur dioxide and to enhanced washout of droplets which condensed about the sulfate particles as nuclei. A portion of these sulfate nuclei may have been contributed by upwind sources.

The different nature of the sub-plume sulfate flux during snowfall is demonstrated by the relationships of sulfate flux to precipitation rate. Both background and sub-plume sulfate washout fluxes in rain and the background flux in snow were linearly related to precipitation rate. However, the sub-plume, sulfate washout flux in snow increased as the square of the precipitation rate. Consequently, there appears to be a unique interaction between the plume and snow or between the plume and precipitation during near-freezing conditions. As a result, if it is assumed that sub-plume sulfate flux minus background sulfate flux can be attributed to the Keystone Station, the washout of sulfur as sulfate, is greater than the washout of sulfur as sulfur dioxide close to the elevated source during snowfall.

It has been shown, that sulfur dioxide washout from distant, major sources and even from a number of minor, disperse sources readily obscures the washout from a major, elevated sulfur dioxide source nearby. This is largely a consequence of the low retention of sulfur dioxide by precipitation after its passage through an elevated plume. Therefore, tall stacks exercise a positive action in reducing the maximum concentration of sulfur dioxide in precipitation. No similar benefit is likely for the washout of sulfate which may be appreciable in the vicinity of the sulfur dioxide source. Higher total sulfur dioxide washout is likely to occur at greater distances where diffusion of the plume results in greater concentration in the near-surface air. It has not been shown where and to what degreee the washout of sulfur dioxide from the Keystone Generating Station is maximized. However, considerable clarification of the complex process of sulfur dioxide washout has been provided, and this new information can be applied toward resolution of the problem.

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APPENDIX A

FIELD DATA SUMMARY

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TABLE A.1

SUMMARY OF FIELD PERIOD I -- OCTOBER-NOVEMBER, 1969

Date	Run No.	Wind[1] Velocity (deg/mph)	SO$_2$ Emission (tons-hr^{-1})	Arcs	Run Time[2]	Sampling[3] Duration (min)	Precip.[4] Rate (mm-hr^{-1})	SO$_2$ Recovery (µmoles)	SO$_2$ Concentration		
									Max	Mean	Min
									(µmole-liter^{-1})		
10-20	1	230/12[5]	13.6	A	2201-2236	80	0.52	4.21	7.1	5.8	0.1
				B	2224-2253	97	0.29	3.46	9.8	7.7	1.8
11-1	2	150/8	12.2	A	0745-0848	118	0.38	1.93	8.8	1.5	0.0
				B	0747-0846	118	0.37	5.07	16.7	3.1	0.2
11-1	3	145/6	12.1	A	0916-1050	99	0.14	0.42	9.0	2.1	0.2
				B	0918-1042	114	0.11	0.48	5.8	2.6	0.1
11-2	4	162/6	11.7	A	0838-0854	61	1.28	16.93	12.3	7.2	2.0
				B	0844-0906	72	0.87	16.79	10.4	7.2	2.2
11-2	5	145/6	10.8	A	0957-1055	104	0.60	11.77	10.8	6.7	1.4
				B	1031-1106	92	0.36	4.71	8.8	4.1	0.4

---

[1] Wind velocity at stack exit, unless otherwise noted.

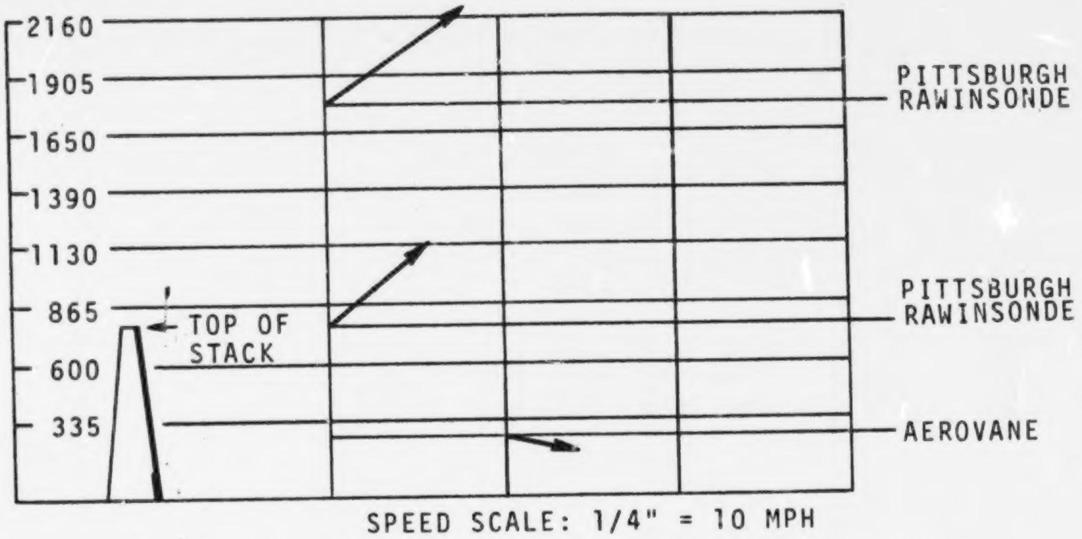
[2] Time of concurrent sampling by all collectors.

[3] Average duration of collector exposure.

[4] Average rate determined from average volume of precipitation collected and average duration of collector exposure.

[5] 1900 EST Pittsburgh rawinsonde.

RUN NO. 1 DATE 10-20-69 TIME 2201-2253



HEIGHT (FT)	TIME →	1900	2100		
2160	PIBAL				
1905	PIBAL				
1775	RAWIN	235/39			
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN	230/30			
600	PIBAL				
335	PIBAL				
300	AERO		280/17		

NOTES: 1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.

2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.

3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.

4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.1 Wind Profiles, Run 1

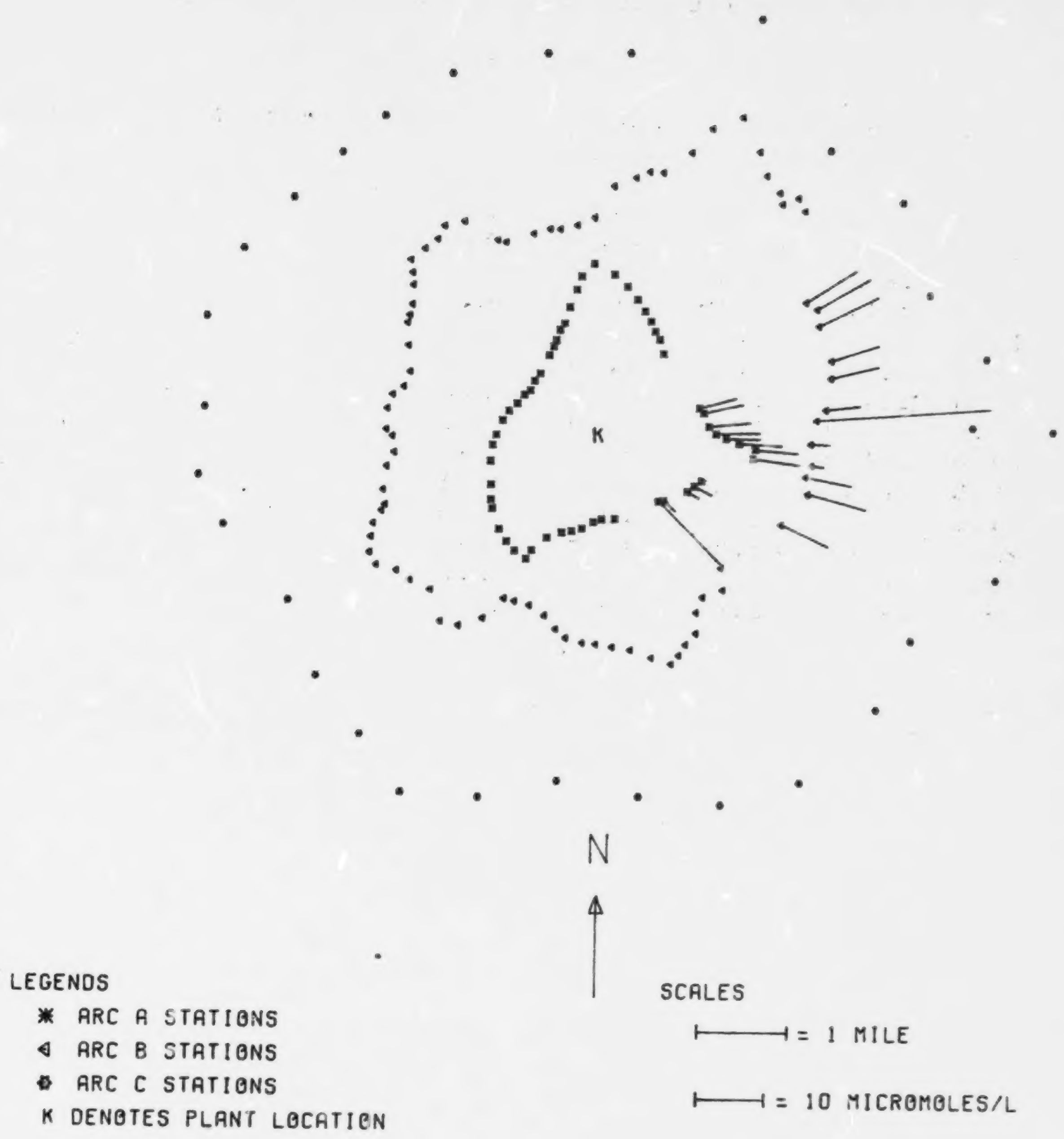

K
N
LEGENDS
✱ ARC A STATIONS
◁ ARC B STATIONS
✱ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.2 Sulfur Dioxide Distribution, Run 1

TABLE A.2

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 1 OCT. 20, 1969 ARC A

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
.0	22:37	23:22	31.0	2.6				
10.0	22:15	23:36	83.0	5.6				
11.0	22:16	23:38	79.5	5.9				
12.0	22:18	23:39	74.0	6.1				
13.0	22:19	23:41	74.0	6.5				
14.0	22:20	23:42	71.0	5.1				
15.0	22:21	22:45	67.0	6.3				
16.0	22:22	23:46	63.0	6.3				
17.0	22:25	23:47	153.5	7.1				
20.0	22:41	23:56	21.0	.1				
21.0	22:42	23:57	19.5	3.0				
22.0	22:44	23:59	17.5	2.0				
25.0	22:46	0:03	24.5	2.3				
26.0	22:47	0:05	19.5	13.0				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

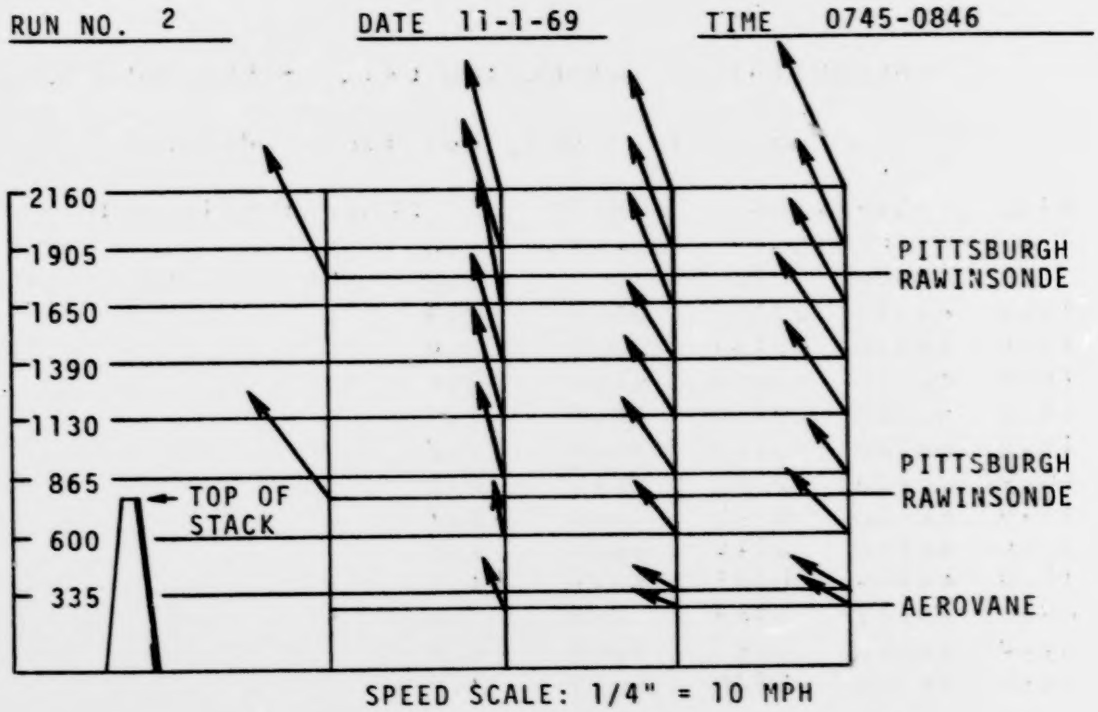
TABLE A.3

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 1 OCT. 20, 1969 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
10.0	22:15	23:53	85.0	8.9				
11.0	22:18	23:57	75.5	9.0				
12.0	22:20	0:01	66.0	9.8				
14.0	22:25	0:06	56.0	7.4				
15.0	22:28	0:09	50.0	7.2				
16.0	22:33	0:12	43.0	5.1				
17.0	22:38	0:15	32.5	25.7				
18.0	22:42	0:18	20.0	2.8				
19.0	22:45	0:21	13.0	1.8				
20.0	22:47	0:24	9.0	6.8				
21.0	22:49	0:27	12.0	8.8				
24.0	22:56	0:36	18.0	7.6				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.



HEIGHT (FT)	TIME →	0700	0725	0823	0930
2160	PIBAL		166/33	162/30	158/35
1905	PIBAL		165/32	162/28	151/27
1775	RAWIN	160/34			
1650	PIBAL		170/30	160/28	153/28
1390	PIBAL		165/27	152/21	147/30
1130	PIBAL		165/27	150/22	147/26
865	PIBAL		165/22	147/21	143/15
775	RAWIN	145/32			
600	PIBAL		166/14	144/16	135/21
335	PIBAL			121/11	123/15
300	AERO		155/12	110/11	120/13

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.3 Wind Profiles, Run 2

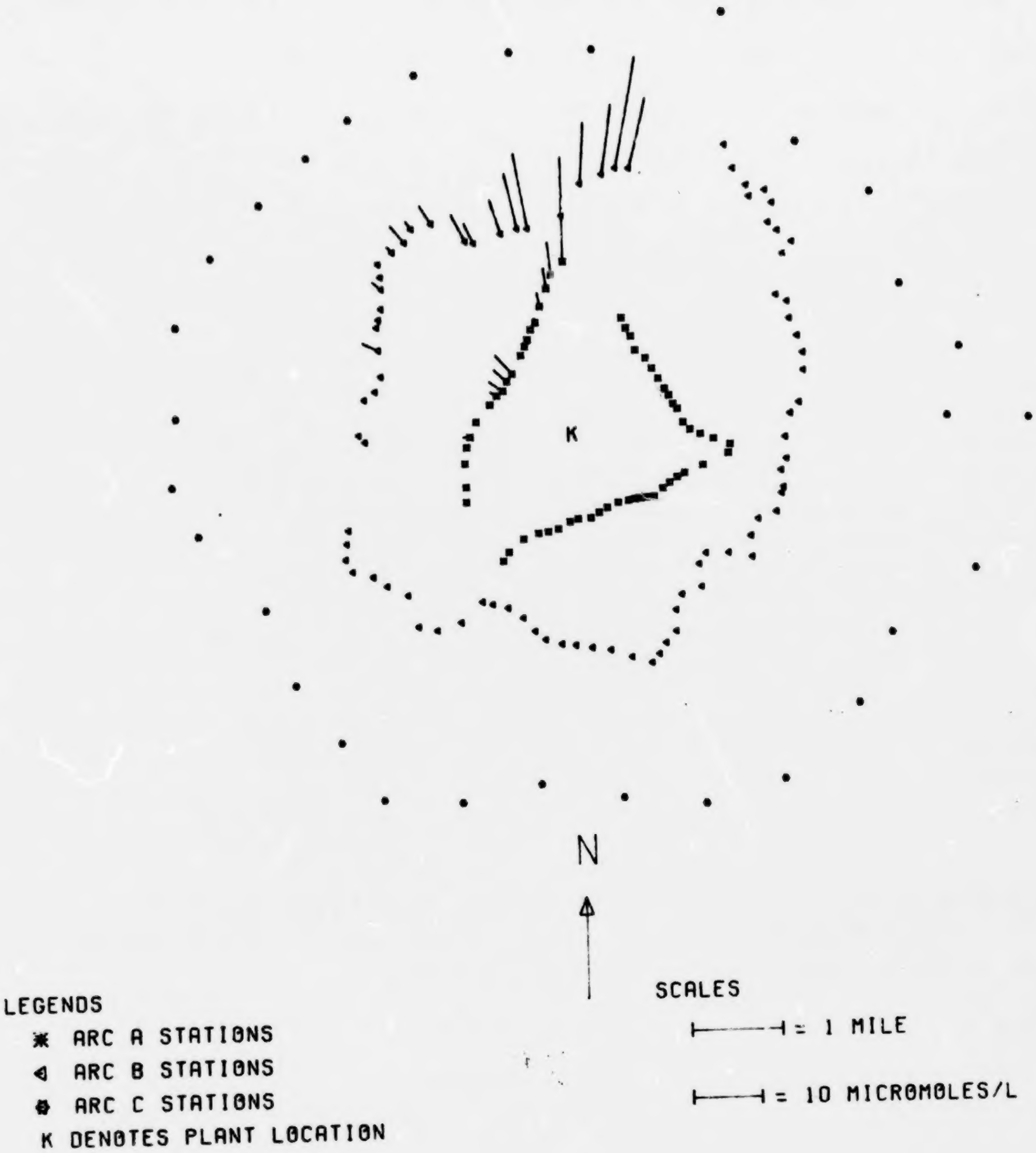

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
⊢—⊣ = 1 MILE
⊢—⊣ = 10 MICROMOLES/L

Figure A.4 Sulfur Dioxide Distribution, Run 2

TABLE A.4

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 2 NOV. 1, 1969 ARC A

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
.0	7:17	8:46	50.0	.0	4.6			4.72
44.0	6:51	8:48	67.0	.1	4.8			
45.0	6:54	8:50	71.0	.2	4.0			
46.0	6:56	8:54	73.0	.1	4.2			
47.0	6:58	8:57	75.0	.2	3.8			
48.0	7:02	8:59	70.0	1.1	4.2			
49.0	6:59	9:01	79.0	.3	4.1			
51.0	7:06	9:04	81.0	.6	4.4			
52.0	7:12	9:07	69.0	1.2	3.4			4.70
53.0	7:20	9:16	69.0	2.5	2.6			
54.0	7:22	9:16	44.0	2.6	3.8			
55.0	7:24	9:21	69.0	3.8	4.2			
56.0	7:25	9:23	60.0	.3	3.4			
57.0	7:26	9:25	67.0	.6	4.2			
58.0	7:27	9:27	64.0	.3	3.4			
59.0	7:36	9:30	51.0	.3	2.8			4.72
60.0	7:40	9:39	54.0	.7	2.5			
61.0	7:41	9:41	54.0	2.1	2.5			
62.0	7:43	9:43	46.0	3.1	2.5			
63.0	7:44	9:44	51.0	4.9	2.6			
64.0	7:45	9:47	52.0	8.8	3.4			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.5

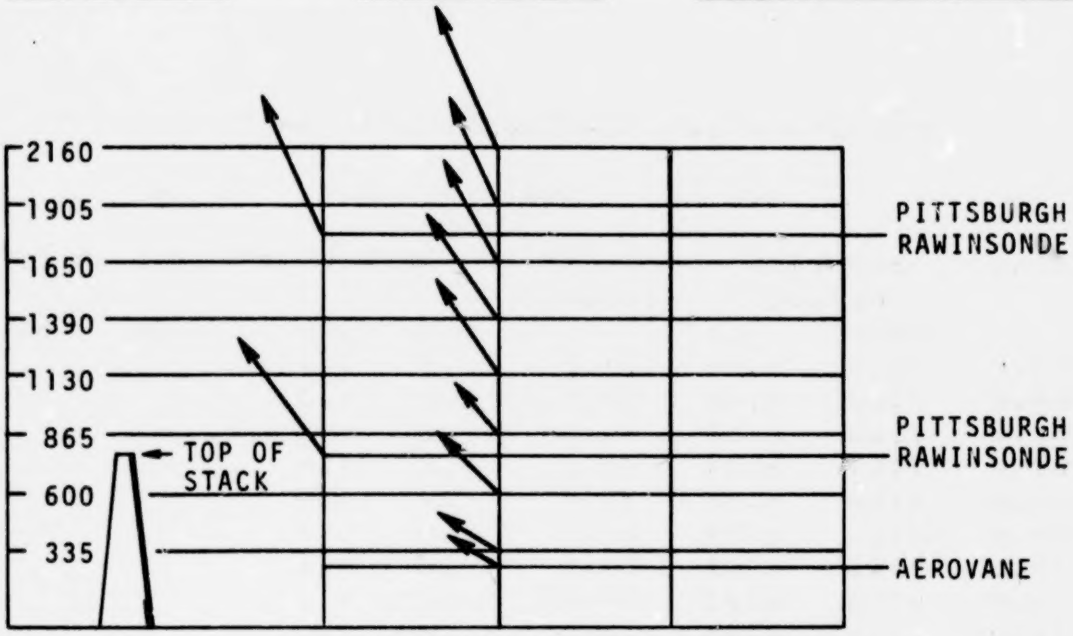
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 2 NOV. 1, 1969 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
63.0	7:00	8:46	74.0	.2	11.2			
64.0	7:02	8:49	72.0	.2	4.3			
66.0	7:05	8:51	79.0	.2	4.2			
67.0	7:07	8:54	70.0	.2	4.4			
68.0	7:08	8:56	70.0	.2	3.8			
69.0	7:10	8:59	66.0	2.6	4.1			
70.0	7:11	9:01	73.0	.2	4.1			
71.0	7:13	9:03	74.0	.2	4.3			4.41
72.0	7:14	9:05	73.0	.2	3.4			
73.0	7:15	9:07	69.0	1.8	4.8			
74.0	7:17	9:15	69.0	.3	4.8			
75.0	7:19	9:18	70.0	.5	5.0			
76.0	7:20	9:21	73.0	1.3	4.4			
77.0	7:22	9:23	66.0	3.3	4.8			
78.0	7:23	9:25	66.0	1.5	4.8			
79.0	7:24	9:27	66.0	3.2	5.6			
80.0	7:26	9:30	65.0	4.5	5.6			4.13
81.0	7:27	9:34	65.0	3.3	5.2			
82.0	7:29	9:36	64.0	5.3	4.7			
83.0	7:31	9:37	62.0	8.4	4.4			
84.0	7:32	9:38	37.0	11.4	4.7			
86.0	7:35	9:42	43.0	8.7	5.8			
87.0	7:38	9:44	46.0	9.1	5.8			
88.0	7:40	9:47	40.0	10.5	5.6			
89.0	7:44	9:50	32.0	16.7	8.0			
90.0	7:47	9:53	39.0	10.8	5.8			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 3 DATE 11-1-69 TIME 0916-1042

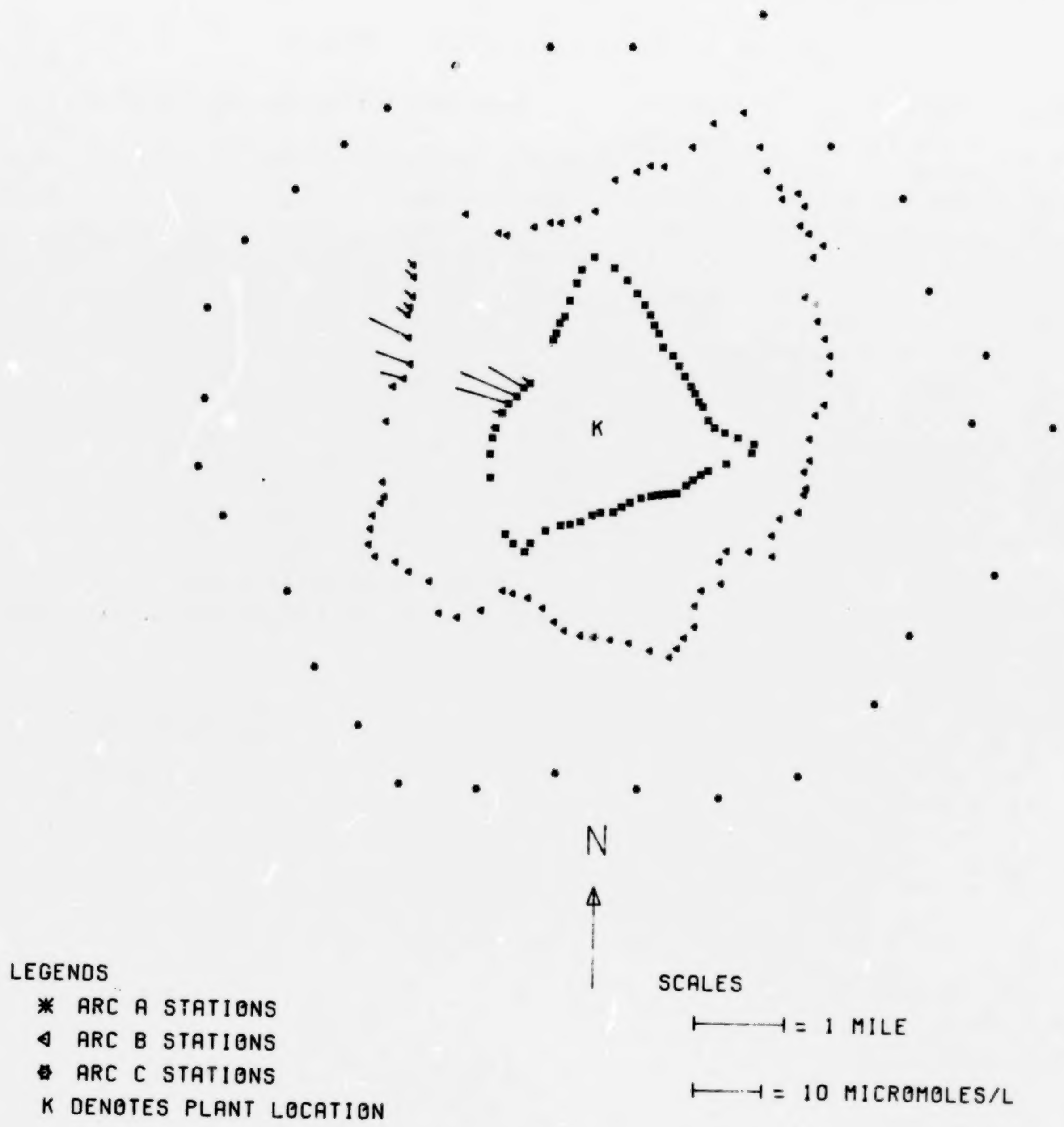


SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	0930		
2160	PIBAL		158/35		
1905	PIBAL		151/27		
1775	RAWIN	160/34			
1650	PIBAL		153/28		
1390	PIBAL		147/30		
1130	PIBAL		147/26		
865	PIBAL		143/15		
775	RAWIN	145/32			
600	PIBAL		135/21		
335	PIBAL		123/15		
300	AERO		120/13		

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.5 Wind Profiles, Run 3



K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
✹ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.6 Sulfur Dioxide Distribution, Run 3

TABLE A.6

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 3 NOV. 1, 1969 ARC A

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	8:47	10:30	29.0	1.2	4.8			4.54
44.0	8:48	10:50	27.0	.0	4.8			
45.0	8:50	10:51	26.0	.2	5.2			
46.0	8:54	10:53	25.0	.3	5.3			
47.0	8:57	10:55	19.0	.2	5.8			
48.0	8:59	10:56	18.0	.8	4.7			
49.0	9:01	10:58	15.0	1.5	4.4			
50.0	9:02	10:59	17.0	8.1				
51.0	9:04	11:01	16.0	9.0				
52.0	9:07	11:09	7.0	6.0				
53.0	9:16	11:15	3.0	14.7				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.7

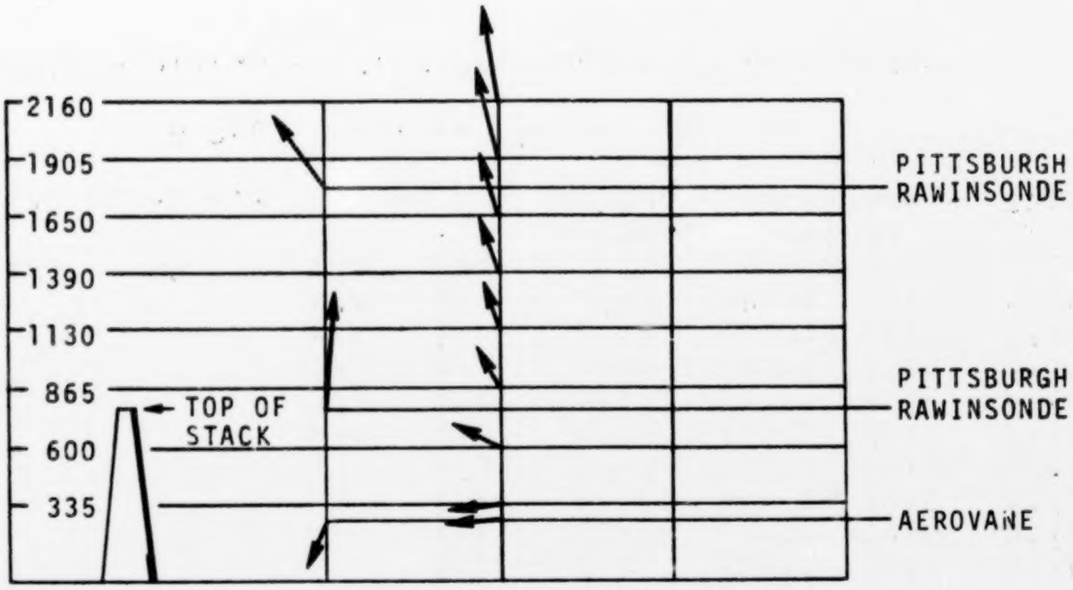
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 3 NOV. 1, 1969 ARC 8

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
63.0	8:46	10:42	26.0	.0	5.8			
64.0	8:49	10:45	26.0	.1	4.6			
66.0	8:51	10:47	23.0	.6	4.3			
67.0	8:54	10:49	28.0	3.6	4.7			
68.0	8:56	10:51	25.0	5.5	4.4			
69.0	8:59	10:53	20.0	6.5				
70.0	9:01	10:55	10.0	2.1				
71.0	9:03	10:57	14.0	1.2				
72.0	9:05	10:59	9.0	1.6				
73.0	9:07	11:02	10.0	1.7				
74.0	9:15	11:04	15.0	1.2				
75.0	9:18	11:06	5.0	.0				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATIO UNITS ARE MILLIGRAMS/L.

RUN NO. 4 DATE 11-2-69 TIME 0838-0906



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	0830		
2160	PIBAL		172/22		
1905	PIBAL		167/21		
1775	RAWIN	145/21			
1650	PIBAL		162/15		
1390	PIBAL		162/13		
1130	PIBAL		162/11		
865	PIBAL		153/9		
775	RAWIN	185/28			
600	PIBAL		118/11		
335	PIBAL		089/12		
300	AERO	020/10	085/11		

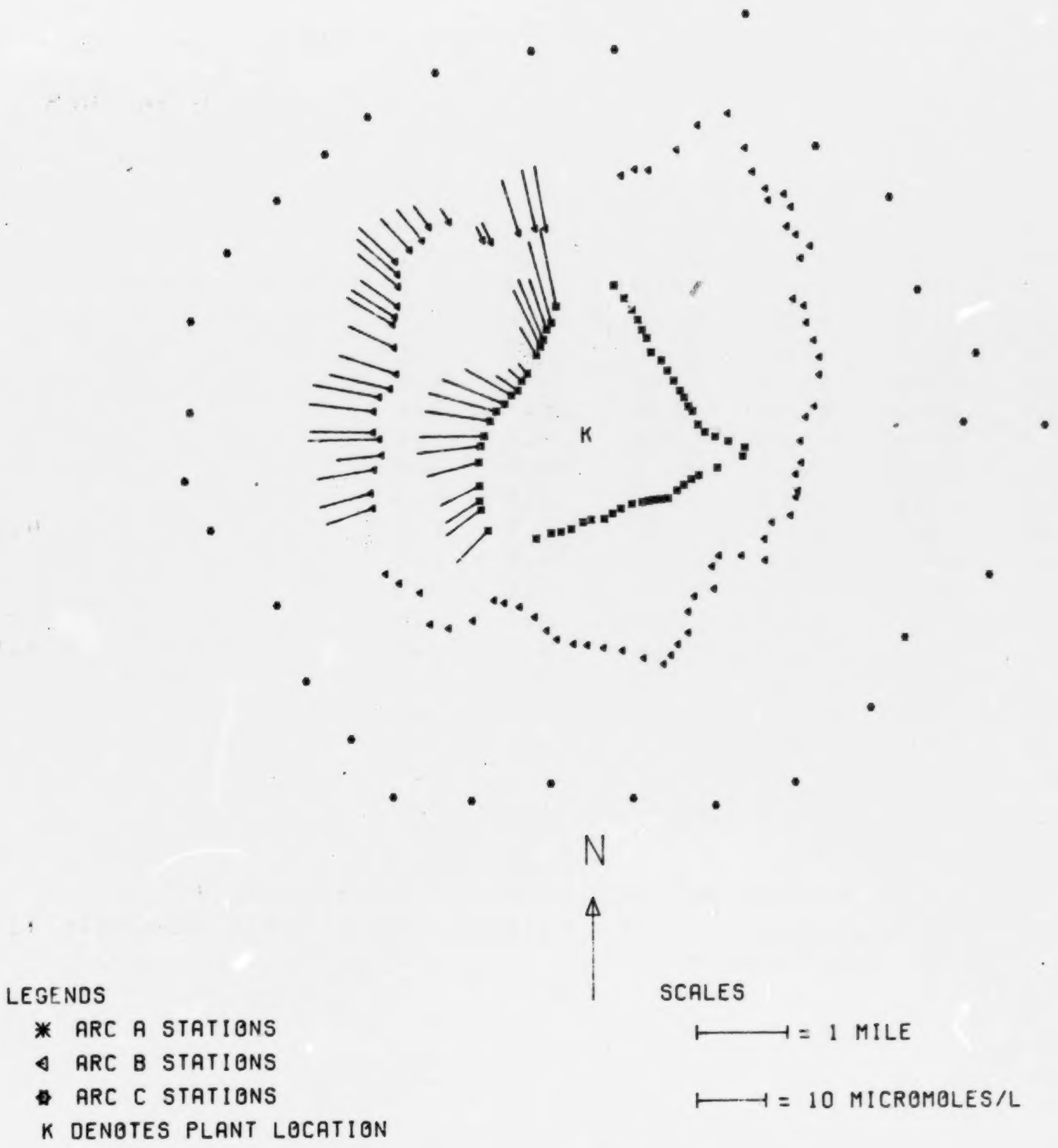
NOTES: 1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.

2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.

3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.

4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.7 Wind Profiles, Run 4



K
N
LEGENDS
✱ ARC A STATIONS
◄ ARC B STATIONS
✿ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
⊢——⊣ = 1 MILE
⊢——⊣ = 10 MICROMOLES/L

Figure A.8 Sulfur Dioxide Distribution, Run 4

TABLE A.8

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 4 NOV. 2, 1969 ARC A

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	7:55	9:46	107.0	8.3	1.9			5.09
42.0	7:55	8:54	88.0	6.5	1.9			
43.0	7:57	8:55	86.0	6.3	2.3			
44.0	7:58	8:57	89.0	5.9	2.1			
45.0	7:59	8:58	82.0	6.4	1.8			
46.0	8:00	9:00	90.0	7.8	1.6			
47.0	8:02	9:02	85.0	9.3	1.6			
48.0	8:03	9:03	100.0	9.4	1.8			
49.0	8:04	9:04	95.0	9.5	1.5			
50.0	8:05	9:06	92.0	10.2	1.6			
51.0	8:06	9:11	100.0	9.6	1.3			
52.0	8:07	9:23	95.0	7.9	1.8			4.08
53.0	8:20	9:28	121.0	3.8	1.8			
54.0	8:21	9:29	141.0	2.6	3.0			
55.0	8:22	9:31	122.0	2.0	3.6			
56.0	8:24	9:33	115.0	4.7	2.3			4.08
57.0	8:33	9:41	117.0	9.1	2.6			
58.0	8:34	9:43	128.0	9.6	2.8			
59.0	8:36	9:44	135.0	7.8	1.1			
60.0	8:37	9:45	122.0	12.3	2.8			
61.0	8:38	9:48	122.0	11.6	2.3			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.9

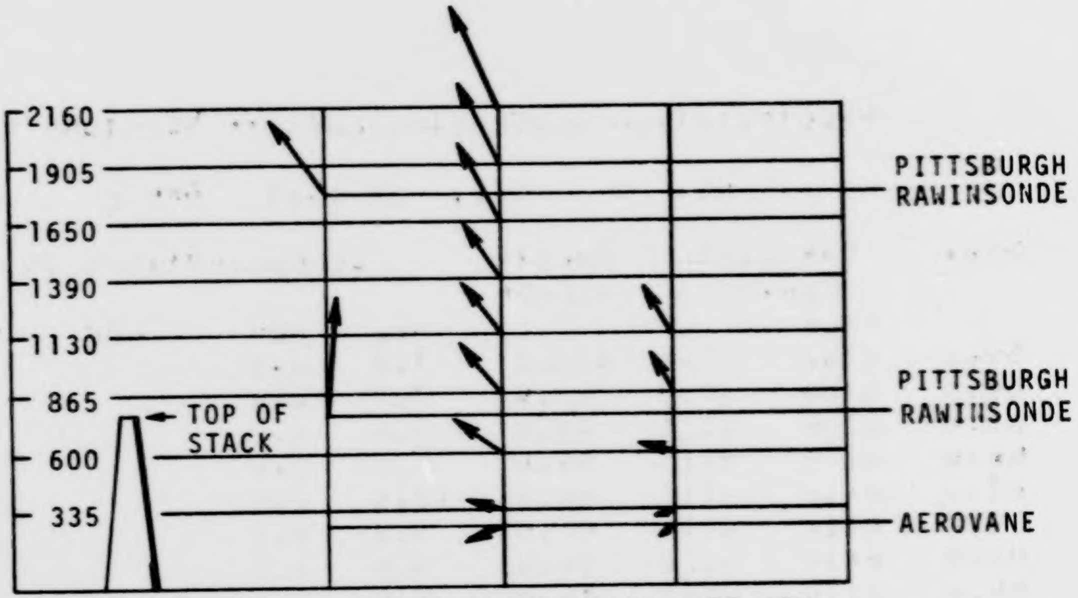
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 4 NOV. 2, 1969 ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
59.0	8:02	9:06	105.0	7.2	2.3			
60.0	8:04	9:09	87.0	7.7	2.8			
61.0	8:06	9:11	91.0	8.4	2.6			
62.0	8:08	9:13	59.0	6.6	2.6			
63.0	8:10	9:16	89.0	10.4	2.6			
64.0	8:12	9:18	80.0	9.2	2.1			
65.0	8:14	9:20	72.0	9.5	2.3			
66.0	8:16	9:22	75.0	9.8	2.3			
67.0	8:18	9:24	76.0	9.1	2.5			4.55
68.0	8:20	9:28	80.0	8.8	2.4			
69.0	8:21	9:31	81.0	7.4	3.0			
70.0	8:23	9:34	74.0	7.8	2.0			
71.0	8:25	9:37	90.0	7.5	3.0			
72.0	8:26	9:39	43.0	6.6	1.0			
73.0	8:28	9:42	84.0	7.6	1.3			
74.0	8:29	9:44	85.0	7.8	.6			
75.0	8:31	9:47	72.0	7.3	.4			
76.0	8:32	9:49	64.0	6.2	.4			4.83
77.0	8:34	9:52	98.0	5.9	3.9			
78.0	8:35	9:54	91.0	3.8	3.0			
79.0	8:37	9:56	103.0	2.4	4.0			
80.0	8:38	9:58	105.0	2.2	3.3			
81.0	8:40	10:00	115.0	3.1	3.5			
82.0	8:41	10:02	131.0	8.2	3.0			
83.0	8:43	10:04	138.0	8.8	2.3			
84.0	8:44	10:07	139.0	9.4	2.3			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 5 DATE 11-2-69 TIME 0957-1106



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	1010	1110	
2160	PIBAL		157/26		
1905	PIBAL		154/21		
1775	RAWIN	145/21			
1650	PIBAL		153/20		
1390	PIBAL		147/17		
1130	PIBAL		144/15	150/13	
865	PIBAL		141/15	150/11	
775	RAWIN	185/28			
600	PIBAL		126/18	115/8	
335	PIBAL		102/8	081/4	
300	AERO		080/10	055/4	

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.9 Wind Profiles, Run 5

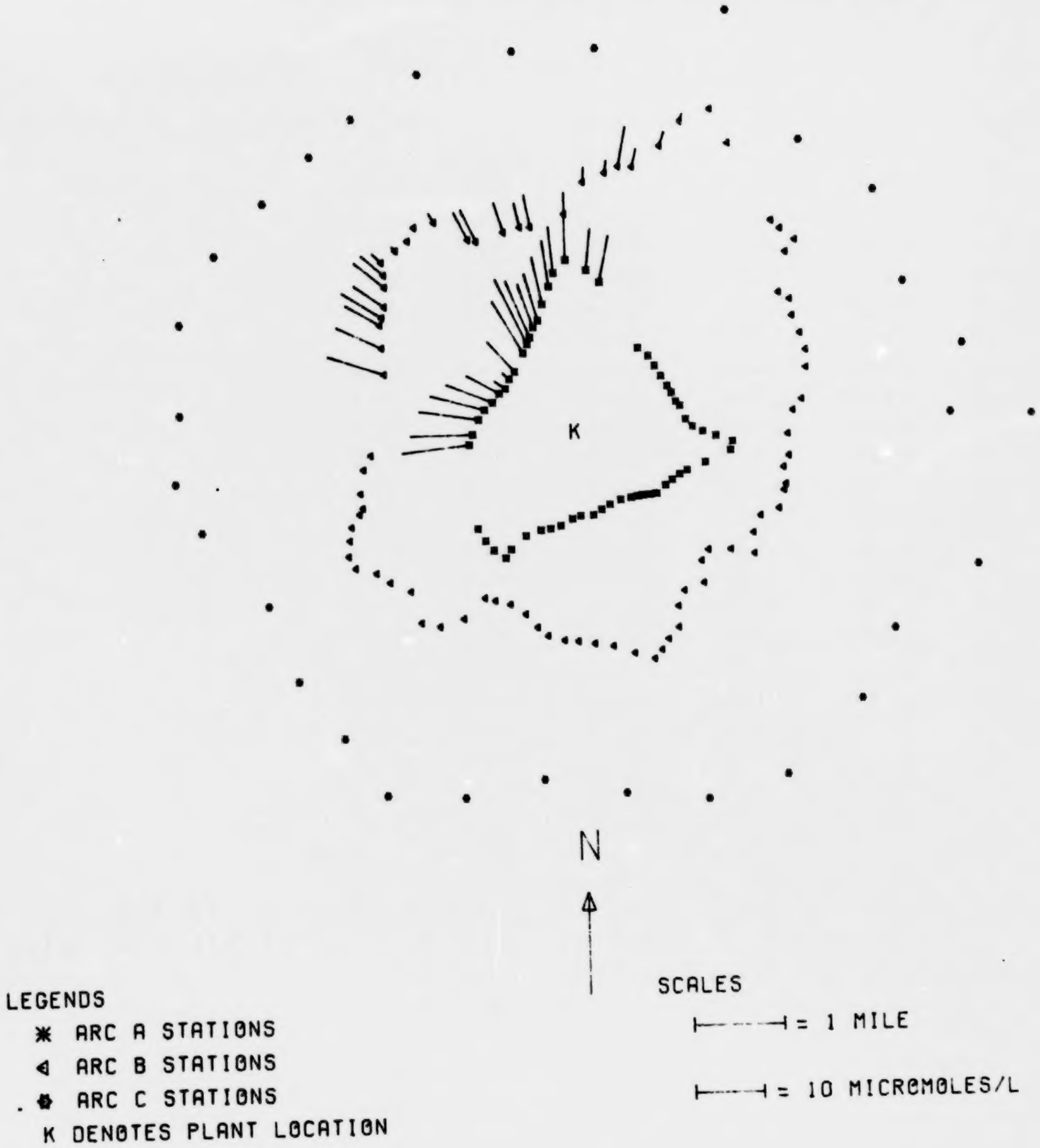

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
⊢——⊣ = 1 MILE
⊢——⊣ = 10 MICROMOLES/L

Figure A.10 Sulfur Dioxide Distribution, Run 5

TABLE A.10

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 5   NOV. 2, 1969   ARC A

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	9:47	12:05	107.0	10.7	3.4			4.62
47.0	9:16	10:55	79.0	9.9	3.0			
48.0	9:17	10:56	84.0	9.2	3.0			
49.0	9:18	10:58	91.0	8.8	3.0			
50.0	9:20	10:59	80.0	8.3	2.8			
51.0	9:21	11:00	82.0	7.3	2.3			
52.0	9:23	11:02	69.0	5.6	3.1			3.59
53.0	9:28	11:14	86.0	2.0	4.6			
54.0	9:29	11:15	105.0	1.4	3.0			
55.0	9:31	11:16	97.0	6.0	2.5			
56.0	9:33	11:18	66.0	8.9	2.9			4.43
57.0	9:41	11:28	91.0	10.8	4.6			
58.0	9:43	11:30	85.0	9.1	3.0			
59.0	9:44	11:31	83.0	6.8	2.8			
60.0	9:45	11:32	84.0	7.2	2.0			
61.0	9:48	11:34	80.0	7.2	2.6			
62.0	9:50	11:36	86.0	6.9	2.5			
63.0	9:51	11:38	80.0	6.9	2.6			
64.0	9:53	11:40	81.0	7.2	2.6			
65.0	9:55	11:42	73.0	6.2	3.0			
66.0	9:57	11:44	69.0	7.0	2.9			

OTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATIO UNITS ARE MILLIGRAMS/L.

TABLE A.11

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 5 NOV. 2, 1969 ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
68.0	9:28	11:06	77.0	8.8	3.0			4.52
69.0	9:31	11:08	66.0	7.4	3.6			
70.0	9:34	11:10	56.0	5.9	3.0			
71.0	9:37	11:12	82.0	7.0	3.6			
72.0	9:39	11:14	46.0	5.5	2.6			
73.0	9:42	11:16	65.0	5.6	3.0			
74.0	9:44	11:18	62.0	4.4	2.5			
75.0	9:47	11:20	17.0	1.9				
76.0	9:49	11:22	54.0	.9	3.4			3.62
77.0	9:52	11:25	64.0	.3	3.3			
78.0	9:54	11:27	69.0	.2	3.5			
79.0	9:56	11:29	57.0	1.6	2.9			
80.0	9:58	11:31	57.0	4.6	3.0			
81.0	10:00	11:33	46.0	5.3	2.6			
82.0	10:02	11:35	43.0	4.7	3.0			
83.0	10:04	11:37	36.0	3.7	3.1			
84.0	10:07	11:39	36.0	4.9	2.6			
86.0	10:15	11:42	25.0	3.2	3.4			
87.0	10:17	11:44	29.0	2.2	4.0			
88.0	10:19	11:46	16.0	1.8				
89.0	10:21	11:47	24.0	6.0	3.4			
90.0	10:23	11:49	26.0	2.7	3.9			
91.0	10:25	11:52	30.0	2.3	3.6			
92.0	10:27	11:54	16.0	1.2				
93.0	10:29	11:56	21.0	.4	3.9			
94.0	10:31	11:58	20.0	.4	3.9			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATIC UNITS ARE MILLIGRAMS/L.

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TABLE A.12

SUMMARY OF FIELD PERIOD II -- FEBRUARY, 1970

Date	Run No.	Wind[1] Velocity (deg/mph)	SO_2 Emission (tons-hr^{-1})	Arcs	Run Time[2]	Sampling[3] Duration (min)	Precip.[4] Rate (mm-hr^{-1})	SO_2 Recovery (μmoles)	SO_2 Concentration Max (μmole-liter^{-1})	SO_2 Concentration Mean (μmole-liter^{-1})	SO_2 Concentration Min (μmole-liter^{-1})
2-3	6	345/8[5]	12.3	A	1229-1430	139	0.31	0.98	1.9	0.8	0.1
				B	1307-1455	131	0.24	1.34	4.9	1.4	0.1
2-9	7	145/9	12.2	A	1029-1135	87	1.63	32.22	12.8	7.6	3.8
				B	1054-1207	96	1.30	10.44	7.2	2.5	0.2
2-9	8	149/13	11.1	A	1201-1315	95	0.56	8.47	9.5	5.3	1.8
				B	1238-1340	92	0.15	2.85	12.1	6.3	1.3
2-10	9	290/10[6]	11.6	A	1012-1115	79	0.61	18.66	13.4	8.3	2.7
				B	1048-1138	86	0.76	19.12	11.8	8.2	4.0
2-10	10	290/10[6]	11.6	A	1133-1247	95	0.84	8.93	8.8	3.6	1.1
				B	1218-1312	97	0.79	14.28	9.8	5.2	2.0
2-10	11	290/10[6]	11.6	A	1309-1444	115	0.42	7.75	7.8	5.1	2.7
				B	1357-1506	119	0.41	10.19	11.1	5.9	1.9
2-14	12	146/8	11.8	B	2015-2124	149	0.06	1.21	3.5	1.1	0.1

---

[1] Wind velocity at stack exit, unless otherwise noted

[2] Time of concurrent sampling by all collectors

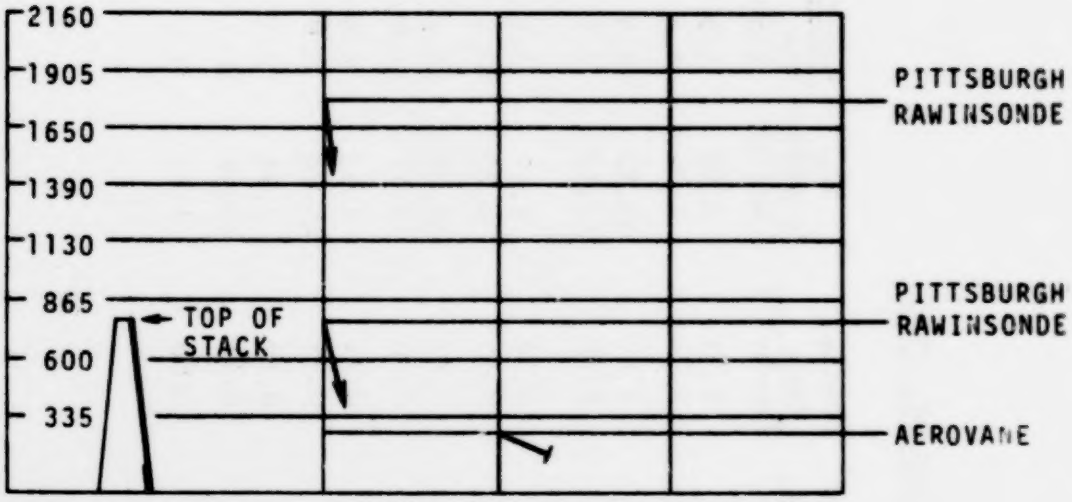
[3] Average duration of collector exposure

[4] Average rate determined from average volume of precipitation collected and average duration of collector exposure.

[5] 0700 EST Pittsburgh rawinsonde.

[6] Best estimate from pibals lost in overcast after 30 seconds.

RUN NO. 6 DATE 2-3-70 TIME 1229-1455



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	1230		
2160	PIBAL				
1905	PIBAL				
1775	RAWIN	350/17			
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN	345/20			
600	PIBAL				
335	PIBAL				
300	AERO		290/u		

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.11 Wind Profiles, Run 6

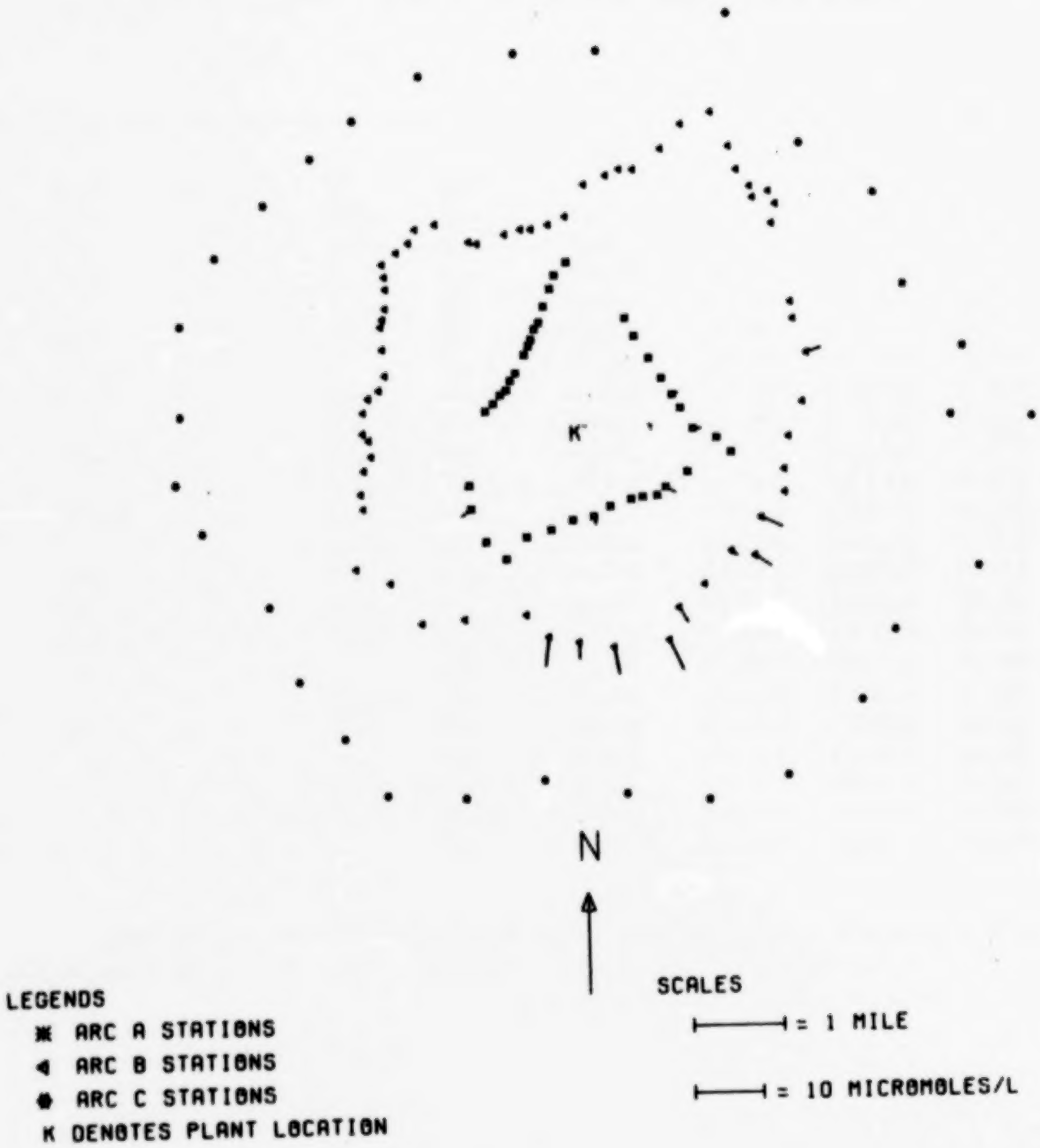

K
N
LEGENDS
* ARC A STATIONS
◄ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.12 Sulfur Dioxide Distribution, Run 6

TABLE A.13

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 6 FEB. 3, 1977 ARC A

STA.	SAMPLING PERIOD FROM	TO.	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
1.0	12:13	14:31	57.0	.2	2.0		.75	4.90
3.0	12:15	14:34	49.0	.2	2.0			
5.0	12:16	14:36	71.0	.1	1.3		.91	4.60
7.0	12:18	14:39	20.0	.3	1.2			
9.0	12:19	14:40	80.0	.9	2.0		.95	4.75
11.0	12:21	14:42	80.0	-.0			1.85	5.55
13.0	12:22	14:45	61.0	1.2	3.0		.91	
15.0	12:13	14:33	51.0	.5	.7			
17.0	12:17	14:36	39.0	.1	.7		1.05	4.75
19.0	12:20	14:38	67.0	.3	2.0			
22.0	12:21	14:40	83.0	1.7	2.6		1.80	5.16
23.0	12:24	14:42	89.0	.8	2.0			
25.0	12:26	14:46	87.0	.7	.7		.92	4.81
27.0	12:27	14:43	72.0	.7	1.3		.95	4.80
31.0	12:13	14:30	87.0	1.3	1.4		1.00	
33.0	12:15	14:33	72.0	.2				4.68
35.0	12:17	14:35	38.0	.2	1.6			
37.0	12:20	14:38	50.0	.3	.7		.82	4.85
39.0	12:21	14:40	39.0	.4	1.0			
41.0	12:24	14:44	33.0	.7	1.3			
43.0	12:26	14:47	90.0	1.9	.7			
45.0	12:26	14:49	83.0	.7				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.14

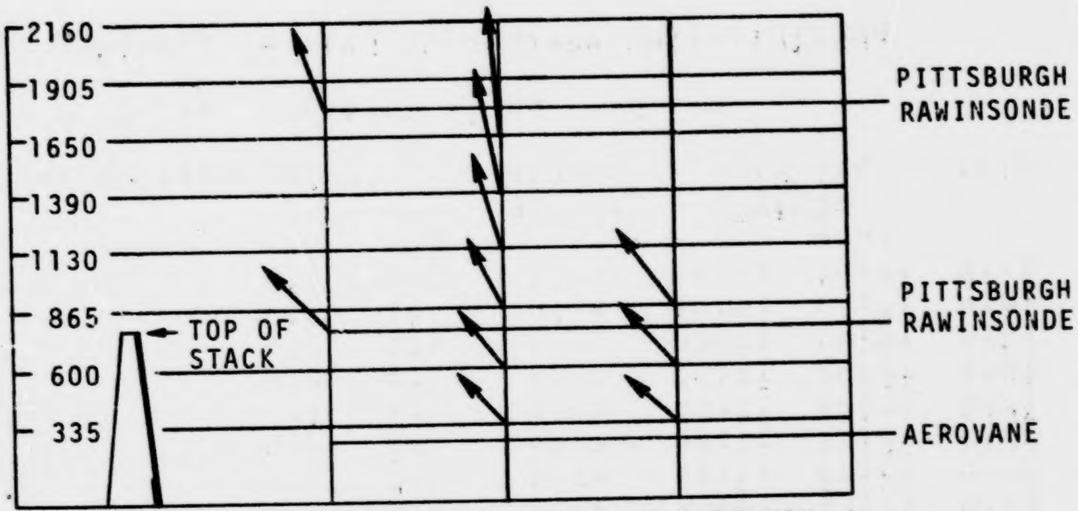
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 6 FEB. 3, 1970 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
11.0	12:51	14:55	42.0	.1	2.2		.91	4.79
12.0	12:53	14:57	46.0	.1	2.9			
14.0	12:55	15:00	58.0	2.3	2.6		.89	4.61
16.0	12:57	15:03	72.0	.3	2.0			
18.0	12:59	15:05	65.0	.1	1.3		.80	4.57
20.0	13:01	15:08	42.0	.1	2.5			
22.0	13:03	15:10	41.0	.2	3.2		.90	4.55
24.0	12:44	14:58	73.0	3.4				
26.0	12:47	15:01	46.0	2.9	1.6		.91	4.67
27.0	12:54	15:03	46.0	1.1	1.6			
30.0	12:59	15:06	41.0	.2	2.2		.92	4.55
32.0	13:01	15:11	45.0	2.6	2.6			
34.0	13:03	15:14	6.0	4.9			1.05	4.55
38.0	13:07	15:19	44.0	4.1	2.0		1.13	4.56
40.0	12:45	15:00	56.0	2.5	1.6			
42.0	12:47	15:03	43.0	4.4	1.0		1.30	5.56
44.0	12:49	15:07	49.0	.4	2.0			
46.0	12:54	15:12	38.0	.3	2.0			
50.0	12:57	15:15	23.0	.3	2.5		1.26	4.60
52.0	12:59	15:19	36.0	.3	2.6			
54.0	13:01	15:23	25.0	.3	2.5		1.10	4.56

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 7 DATE 2-9-70 TIME 1029-1207



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	0915	1119	
2160	PIBAL				
1905	PIBAL				
1775	RAWIN	160/21			
1650	PIBAL		178/30		
1390	PIBAL		171/28		
1130	PIBAL		166/23		
865	PIBAL		154/17	145/21	
775	RAWIN	135/20			
600	PIBAL		143/16	138/19	
335	PIBAL		138/16	132/15	
300	AERO				

NOTES: 1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.

2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.

3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.

4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.13 Wind Profiles, Run 7

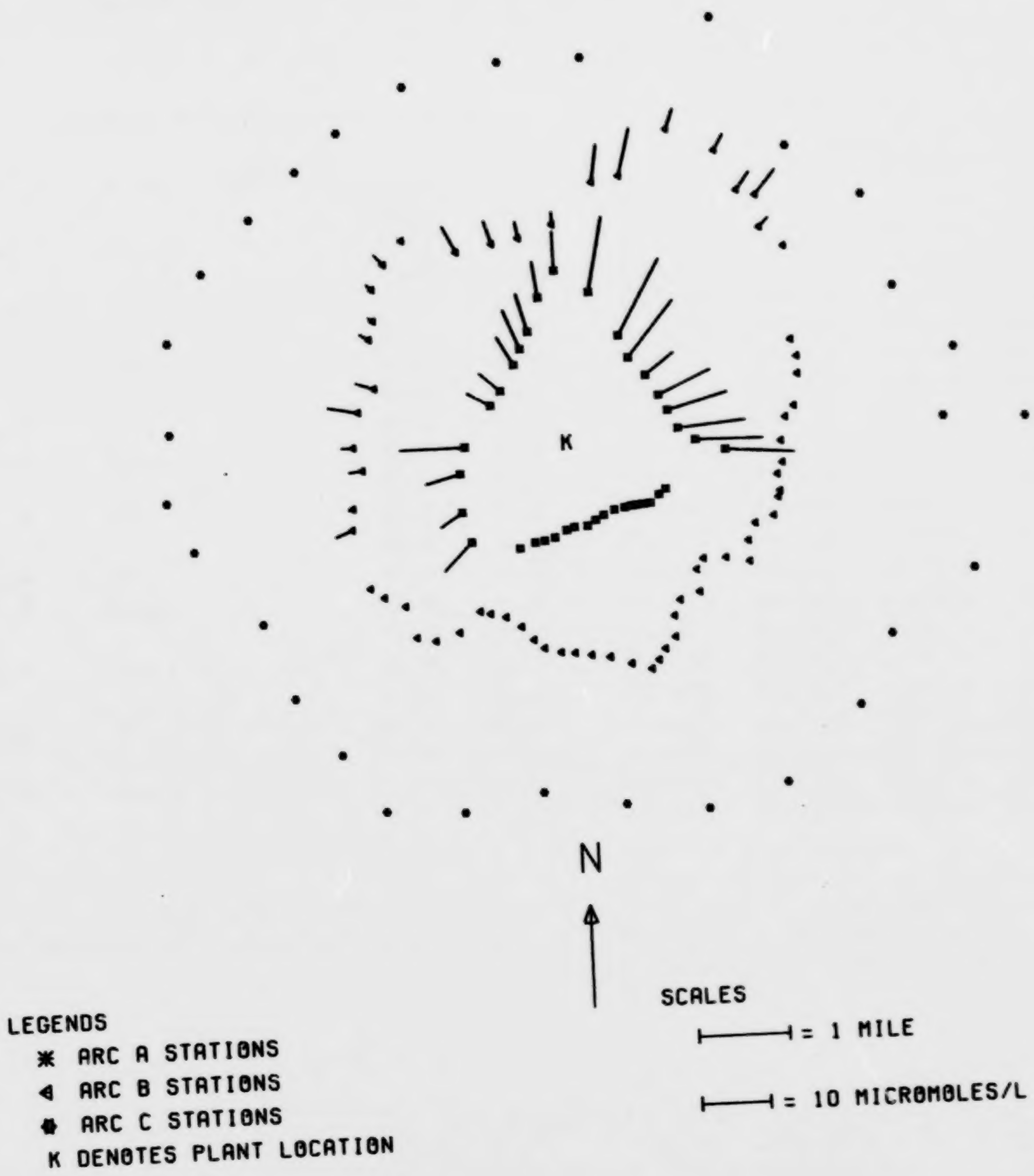

K
N
SCALES
= 1 MILE
= 10 MICROMOLES/L
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION

Figure A.14 Sulfur Dioxide Distribution, Run 7

TABLE A.15

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 7 FEB. 9, 1970 ARC A

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	10:19	11:45	134.5	12.8	9.3		.66	4.61
4.0	10:21	11:46	155.5	10.7	3.9			
6.0	10:22	11:48	174.5	5.3	5.3		.88	5.10
8.0	10:23	11:51	223.0	8.4	5.3			
10.0	10:25	11:57	195.5	9.1	3.3		.60	4.50
12.0	10:26	11:54	270.0	9.9	3.2			
14.0	10:27	11:59	374.0	9.8	4.5		.52	4.56
16.0	10:29	12:01	495.0	10.0	3.8		.61	4.20
30.0	10:22	11:36	241.0	4.0	3.3			
42.0	10:11	11:38	170.5	5.8	3.5		.42	4.91
44.0	10:13	11:41	160.5	3.8	3.5			
46.0	10:14	11:43	195.5	5.2	3.5		.76	4.50
48.0	10:16	11:45	184.0	9.4	6.9		.43	4.88
52.0	10:19	11:49	205.0	3.9	16.5			
54.0	10:24	11:51	36.0	4.0	9.7		1.15	4.41
56.0	10:21	11:55	207.5	4.8	4.5			
58.0	10:22	11:56	183.0	6.3	4.4		1.17	4.40
60.0	10:11	11:35	166.0	5.9	5.1			
62.0	10:13	11:37	179.0	5.4	4.6		1.20	4.66
64.0	10:15	11:37	162.5	5.6	7.0			
66.0	10:17	11:42	148.5	11.3	3.3			

OTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.16

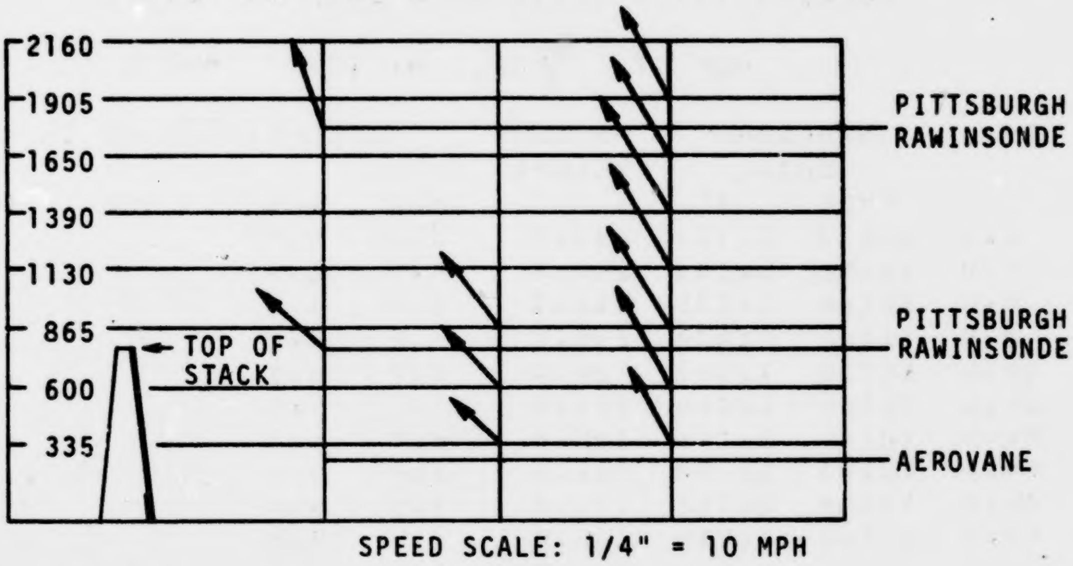
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 7 FEB. 9, 1970 ARC B

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	SO2	SO4	NO2	NO3	PH
2.0	10:53	12:31	213.5	3.3	4.5			
4.0	10:56	12:33	206.0	4.7	5.9		.76	4.60
6.0	11:00	12:35	216.5	1.9	4.3			
8.0	11:02	12:38	246.0	.2	4.5		.43	4.51
58.0	10:36	12:07	124.0	2.7	5.1		.65	4.30
60.0	10:38	12:10	187.0	.7	5.9			
62.0	10:40	12:12	155.0	2.0	5.7		.42	4.35
64.0	10:43	12:15	161.0	1.8	4.5		1.14	4.23
66.0	10:44	12:18	130.5	4.5	4.7			
68.0	10:45	12:19	180.0	2.9	4.5			
70.0	10:47	12:22	190.5	1.6	4.7		.43	4.40
72.0	10:48	12:24	202.0	.9	8.9			
74.0	10:51	12:27	156.5	1.1	5.8		.32	4.39
76.0	10:53	12:30	156.5	2.0	4.5			
78.0	10:54	12:32	160.0	.8	5.1		.44	4.45
80.0	10:35	12:10	185.0	4.3	5.1			
82.0	10:37	12:12	216.0	3.6	5.1		.87	4.35
84.0	10:38	12:15	207.0	2.5	3.3			
86.0	10:40	12:17	170.0	1.8	5.1		.88	4.60
88.0	10:42	12:20	147.5	5.6	3.5			
90.0	10:44	12:22	149.0	7.2	4.4		.88	4.45
92.0	10:46	12:25	172.0	3.2	3.8			
94.0	10:50	12:28	170.0	2.7	3.8		.82	4.51

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 8 DATE 2-9-70 TIME 1201-1340



HEIGHT (FT)	TIME →	0700	1119	1310	
2160	PIBAL				
1905	PIBAL			156/25	
1775	RAWIN	160/21			
1650	PIBAL			154/28	
1390	PIBAL			151/30	
1130	PIBAL			150/27	
865	PIBAL		145/21	149/29	
775	RAWIN	135/20			
600	PIBAL		138/19	152/27	
335	PIBAL		132/15	153/20	
300	AERO				

NOTES:

1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.15 Wind Profiles, Run 8

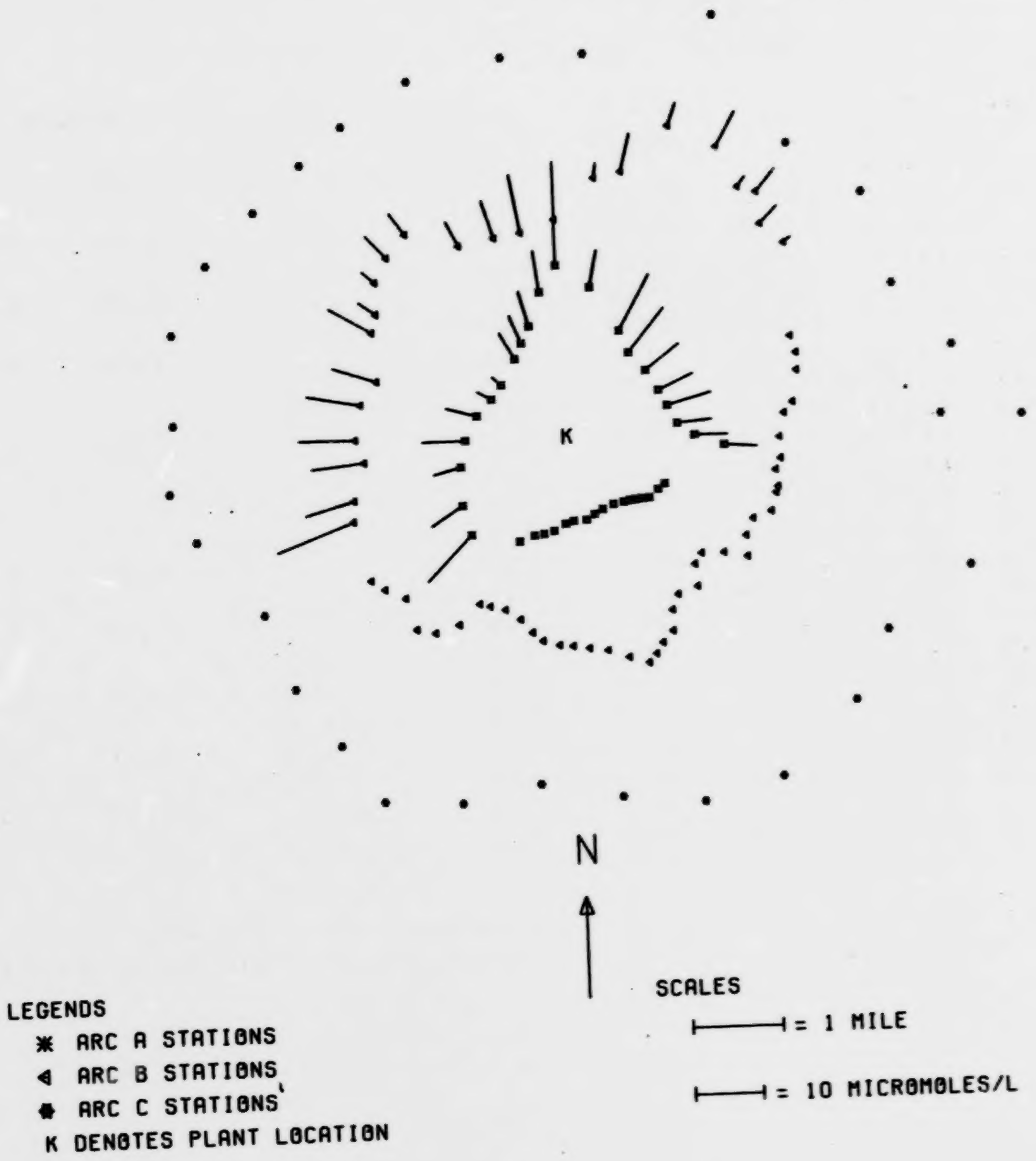

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.16 Sulfur Dioxide Distribution, Run 8

TABLE A.17

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 8 FEB. 9, 1970 ARC A

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	11:45	13:22	72.0	9.5				
4.0	11:46	13:24	79.0	8.4			1.28	4.50
6.0	11:48	13:26	89.0	6.3				
8.0	11:51	13:28	86.0	5.6			1.36	5.20
10.0	11:57	13:29	55.0	6.7				
12.0	11:54	13:30	74.0	5.1			1.72	4.30
14.0	11:59	13:32	56.0	4.8				
16.0	12:01	13:34	59.0	4.8				
30.0	11:40	14:20	117.0	4.4			.66	4.15
42.0	11:38	13:15	85.0	9.4				
44.0	11:41	13:17	92.0	5.5				
46.0	11:43	13:19	24.0	4.1				
48.0	11:45	13:22	119.0	6.3			1.29	3.90
50.0	11:47	13:24	84.0	4.7				
52.0	11:49	13:26	94.0	2.4			.99	3.95
54.0	11:51	13:27	75.0	1.8				
56.0	11:55	13:30	65.0	4.5			.82	4.15
58.0	11:56	13:31	54.0	4.5				
60.0	11:35	13:15	56.0	5.4			1.22	4.10
62.0	11:38	13:16	66.0	6.2				
64.0	11:40	13:19	54.0	6.4			1.15	4.50
66.0	11:42	13:22	50.0	5.6				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.18

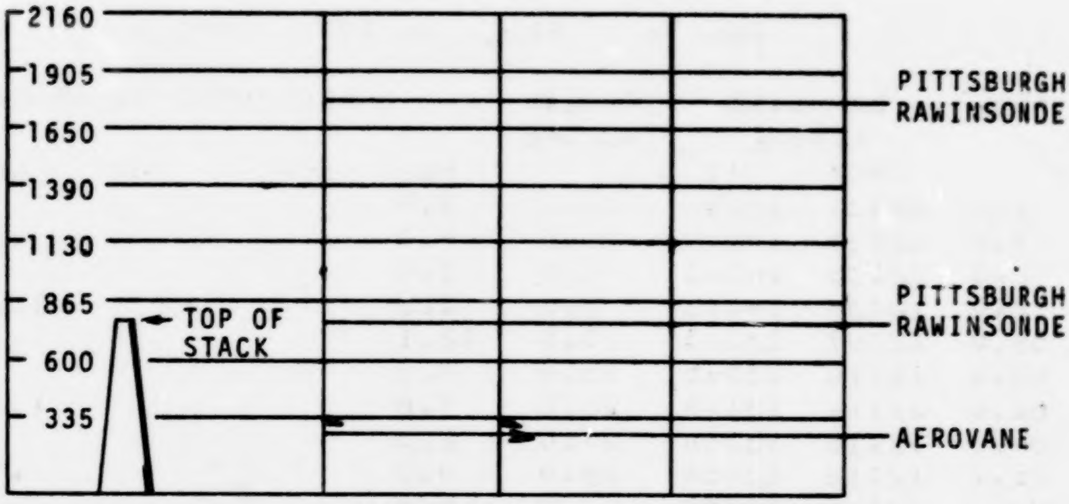
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 8 FEB. 9, 1970 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	12:31	13:58	10.0	1.9				
4.0	12:33	14:00	15.0	4.3			.85	
6.0	12:35	14:03	5.0	3.6				
8.0	12:38	14:05	5.0	1.3			1.31	
58.0	12:07	13:43	27.0	12.1			1.34	3.91
60.0	12:10	13:45	25.0	7.5				
62.0	12:12	13:48	26.0	7.8			1.11	3.90
64.0	12:15	13:50	27.0	8.3				
66.0	12:18	13:54	28.0	8.0			.90	3.90
68.0	12:19	13:56	27.0	6.8				
70.0	12:22	13:59	27.0	7.3			1.06	3.90
72.0	12:24	14:01	20.0	3.1				
74.0	12:27	14:05	20.0	2.5			1.21	3.50
76.0	12:30	14:08	21.0	4.5				
78.0	12:32	14:10	16.0	3.9			1.46	
80.0	12:10	13:40	22.0	4.1				
82.0	12:12	13:41	27.0	5.9			1.11	
84.0	12:15	13:44	21.0	8.8				
86.0	12:17	13:46	16.0	8.6				
88.0	12:20	13:49	7.0	2.2				
90.0	12:22	13:50	19.0	5.8			1.21	4.15
92.0	12:25	13:53	20.0	3.6				
94.0	12:28	13:55	22.0	6.0			.99	4.15

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 9 DATE 2-10-70 TIME 1012-1138



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0930	1040		
2160	PIBAL				
1905	PIBAL				
1775	RAWIN				
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN				
600	PIBAL				
335	PIBAL	282/6.0	293/5.0		
300	AERO		280/8		

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.17 Wind Profiles, Run 9

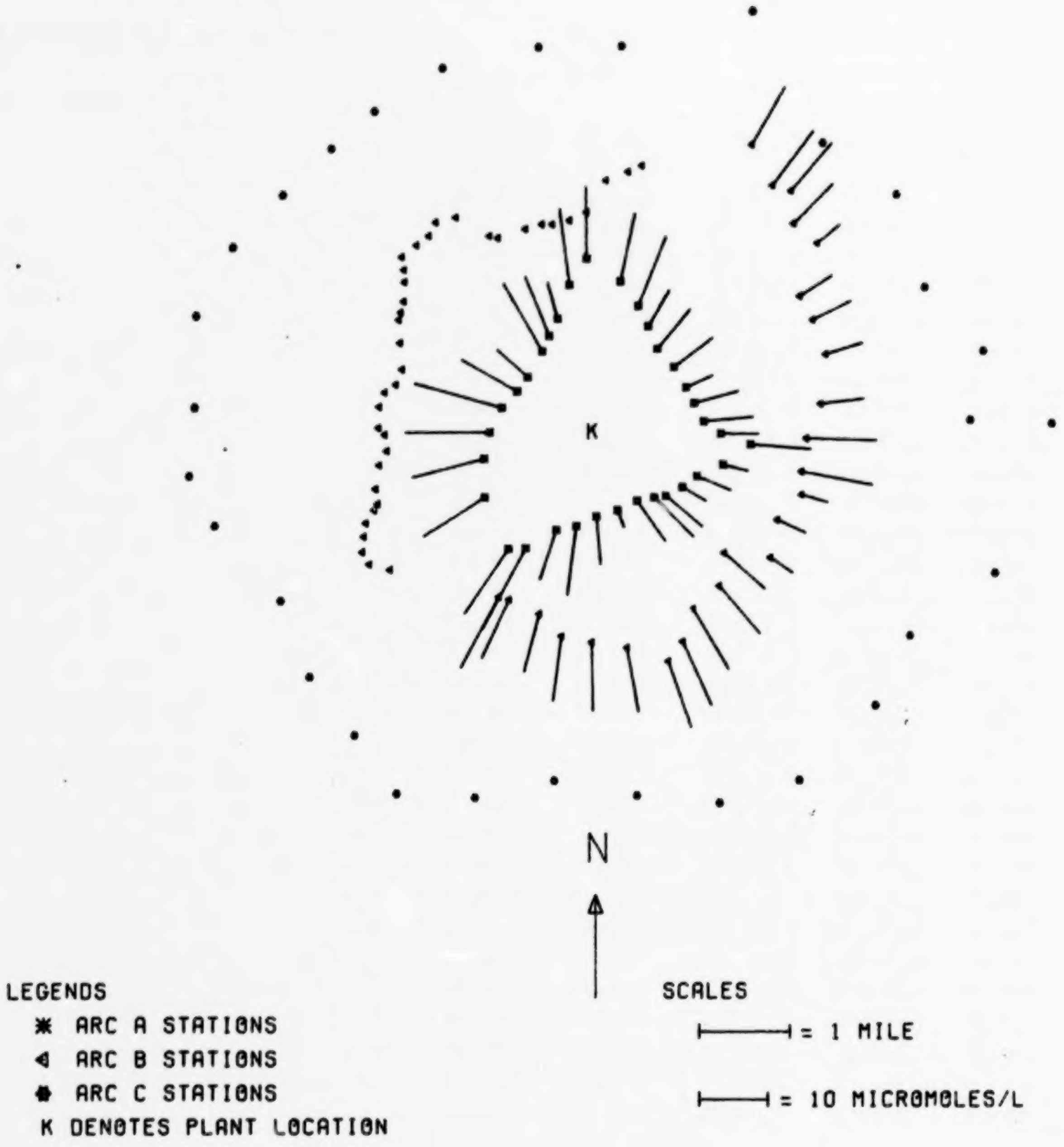

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.18 Sulfur Dioxide Distribution, Run 9

TABLE A.19

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 9 FEB. 10, 1970 ARC A

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
2.0	10:02	11:20	69.0	6.1				
4.0	10:03	11:21	48.0	7.5				
6.0	10:04	11:23	29.0	7.2				
8.0	10:05	11:25	70.0	4.3				
10.0	10:06	11:26	66.0	6.7				
12.0	10:07	11:28	60.0	7.2				
14.0	10:09	11:29	65.0	5.5				
16.0	10:10	11:31	59.0	8.6				
18.0	9:56	11:15	96.0	3.8				
20.0	9:57	11:17	96.0	5.4				
22.0	10:01	11:19	38.0	4.0				
24.0	10:02	11:21	44.0	7.0				
26.0	10:04	11:22	63.0	8.2				
28.0	10:05	11:24	82.0	7.3				
30.0	10:06	11:26	79.0	2.7				
32.0	10:08	11:27	82.0	7.1				
34.0	10:09	11:29	65.0	10.3				
36.0	10:10	11:30	65.0	7.7				
38.0	10:12	11:33	45.0	13.4				
40.0	9:55	11:15	75.0	11.5				
44.0	9:57	11:17	70.0	10.6				
46.0	9:59	11:20	66.0	10.8				
48.0	10:00	11:22	76.0	12.3				
50.0	10:02	11:23	72.0	13.2				
52.0	10:03	11:24	74.0	9.3				
54.0	10:04	11:26	80.0	6.0				
56.0	10:05	11:28	76.0	11.5				
58.0	10:06	11:29	78.0	9.4				
60.0	10:07	11:31	69.0	5.6				
62.0	10:08	11:33	72.0	11.3				
64.0	9:57	11:15	84.0	10.6				
66.0	9:59	11:16	71.0	10.3				
68.0	10:00	11:18	68.0	11.0				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.20

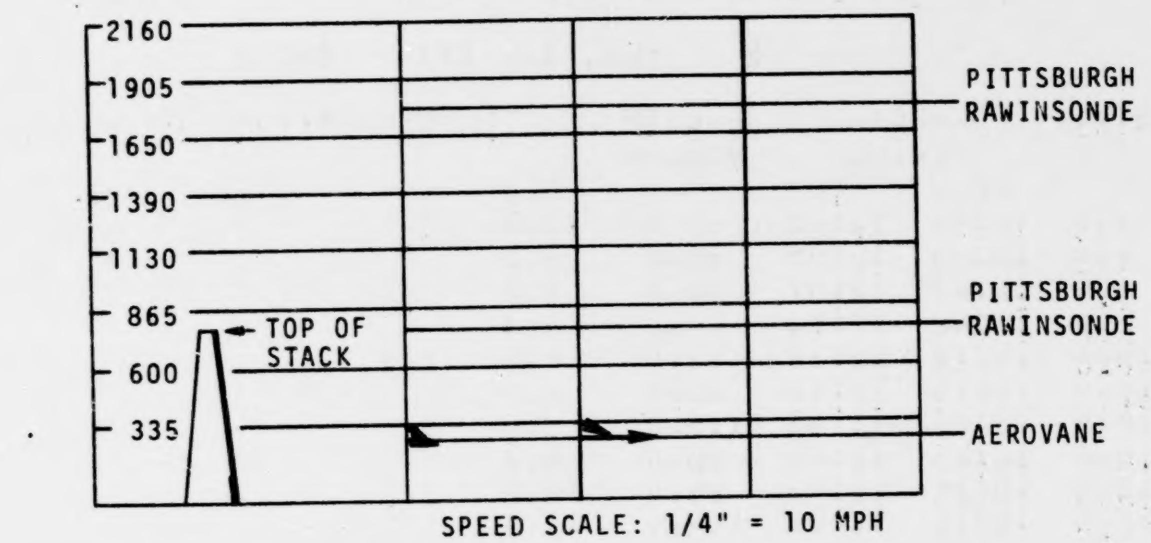
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 9 FEB. 10, 1970 ARC B

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	10:43	12:03	83.0	10.0	3.1			
4.0	10:45	12:05	69.0	9.2				
6.0	10:47	12:07	90.0	8.2	3.1			
8.0	10:48	12:10	80.0	4.3				
10.0	10:16	11:38	91.0	5.6	2.9			
12.0	10:19	11:40	85.0	6.2				
14.0	10:20	11:43	115.0	5.6	3.2			
16.0	10:23	11:45	88.0	6.3				
18.0	10:25	11:47	85.0	10.2	2.2			
20.0	10:18	11:42	104.0	10.4				
22.0	10:21	11:44	85.0	4.0	9.3			
24.0	10:22	11:47	103.0	4.5				
26.0	10:24	11:50	116.0	4.0	6.3			
28.0	10:27	11:52	107.0	8.0				
30.0	10:29	11:56	112.0	9.2	3.7			
32.0	10:31	11:58	104.0	10.3				
34.0	10:33	12:02	79.0	10.3	3.7			
36.0	10:35	12:03	111.0	10.3				
38.0	10:36	12:06	87.0	9.6	3.2			
40.0	10:38	12:08	100.0	10.1				
42.0	10:39	12:11	88.0	9.6	5.4			
44.0	10:41	12:13	100.0	8.8				
46.0	10:43	12:17	100.0	9.5	4.4			
47.0	10:45	12:18	90.0	11.8				
94.0	10:40	11:59	73.0	9.8				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 10 DATE 2-10-70 TIME 1133-1312


2160
1905
1650
1390
1130
865
600
335
TOP OF STACK
PITTSBURGH RAWINSONDE
PITTSBURGH RAWINSONDE
AEROVANE
SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	1040	1400		
2160	PIBAL				
1905	PIBAL				
1775	RAWIN				
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN				
600	PIBAL				
335	PIBAL	293/5	287/10		
300	AERO	280/8	270/17		

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.19 Wind Profiles, Run 10

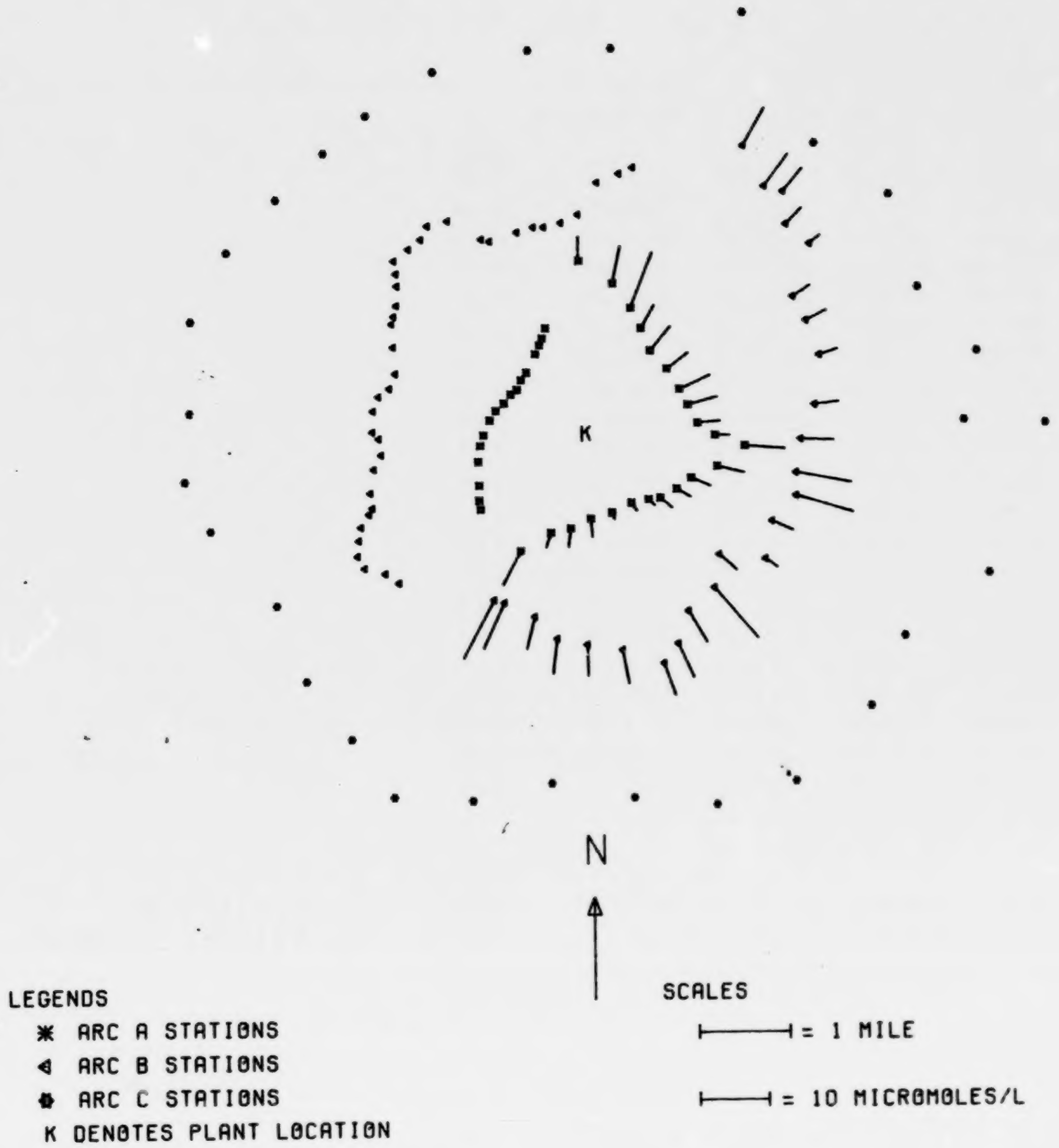

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.20 Sulfur Dioxide Distribution, Run 10

TABLE A.21

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 10   FEB. 10, 1970   ARC A

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO_2	SO_4	NO_2	NO_3	PH
2.0	11:20	12:52	98.0	3.9				
4.0	11:21	12:55	121.0	4.6				
6.0	11:23	12:57	105.0	3.9				
8.0	11:25	12:59	118.0	4.9				
10.0	11:26	13:00	134.0	4.4				
12.0	11:28	13:02	125.0	3.3				
14.0	11:29	13:03	48.0	2.1				
16.0	11:31	13:05	118.0	5.8				
18.0	11:15	12:50	115.0	4.0				
20.0	11:17	12:51	98.0	3.1				
22.0	11:19	12:53	109.0	2.3				
24.0	11:21	12:55	126.0	2.3				
26.0	11:22	12:57	140.0	1.3				
28.0	11:24	12:59	115.0	1.5				
30.0	11:26	13:01	130.0	1.1				
32.0	11:27	13:03	112.0	2.7				
34.0	11:29	13:05	158.0	2.8				
36.0	11:30	13:07	145.0	2.3				
38.0	11:33	13:09	111.0	5.6				
64.0	11:15	12:47	96.0	3.6				
66.0	11:16	12:50	107.0	5.6				
68.0	11:18	12:52	92.0	8.8				

NOTE: VOLUME UNIT IS ML. SO_2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATIO
UNITS ARE MILLIGRAMS/L.

TABLE A.22

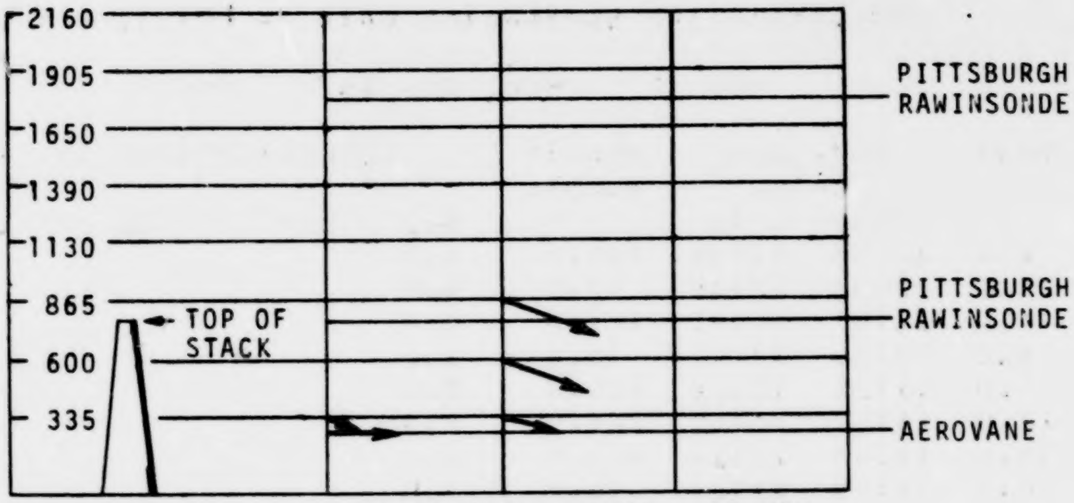
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 10   FEB. 10, 1970   ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
2.0	12:03	13:36	139.0	5.9				4.10
4.0	12:05	13:38	97.0	4.4				
6.0	12:07	13:41	127.0	3.3				3.90
8.0	12:10	13:43	75.0	2.0				
10.0	11:38	13:12	135.0	3.0				4.70
12.0	11:40	13:15	121.0	3.3				
14.0	11:43	13:17	153.0	2.8				4.15
16.0	11:45	13:20	96.0	3.5				
18.0	11:47	13:22	141.0	4.8				4.40
20.0	11:42	13:17	150.0	8.2				
22.0	11:44	13:20	126.0	6.7				3.80
24.0	11:47	13:23	89.0	3.4				
26.0	11:50	13:27	146.0	2.2				4.10
28.0	11:52	13:29	117.0	3.5				
30.0	11:56	13:32	106.0	4.6				4.30
32.0	11:58	13:35	125.0	5.4				
34.0	12:02	13:38	67.0	5.5				4.00
36.0	12:03	13:40	108.0	5.1				
38.0	12:06	13:43	113.0	5.1				4.00
40.0	12:08	13:45	115.0	4.6				
42.0	12:11	13:48	100.0	5.2				3.90
44.0	12:13	13:51	112.0	4.9				
46.0	12:17	13:53	98.0	7.4				4.10
47.0	12:18	13:55	62.0	9.7				
94.0	11:59	13:33	106.0	6.4				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 11 DATE 2-10-70 TIME 1309-1506



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	1400	1515		
2160	PIBAL				
1905	PIBAL				
1775	RAWIN				
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL		290/24		
775	RAWIN				
600	PIBAL		289/22		
335	PIBAL	287/10	282/16		
300	AERO	270/17			

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.21 Wind Profiles, Run 11

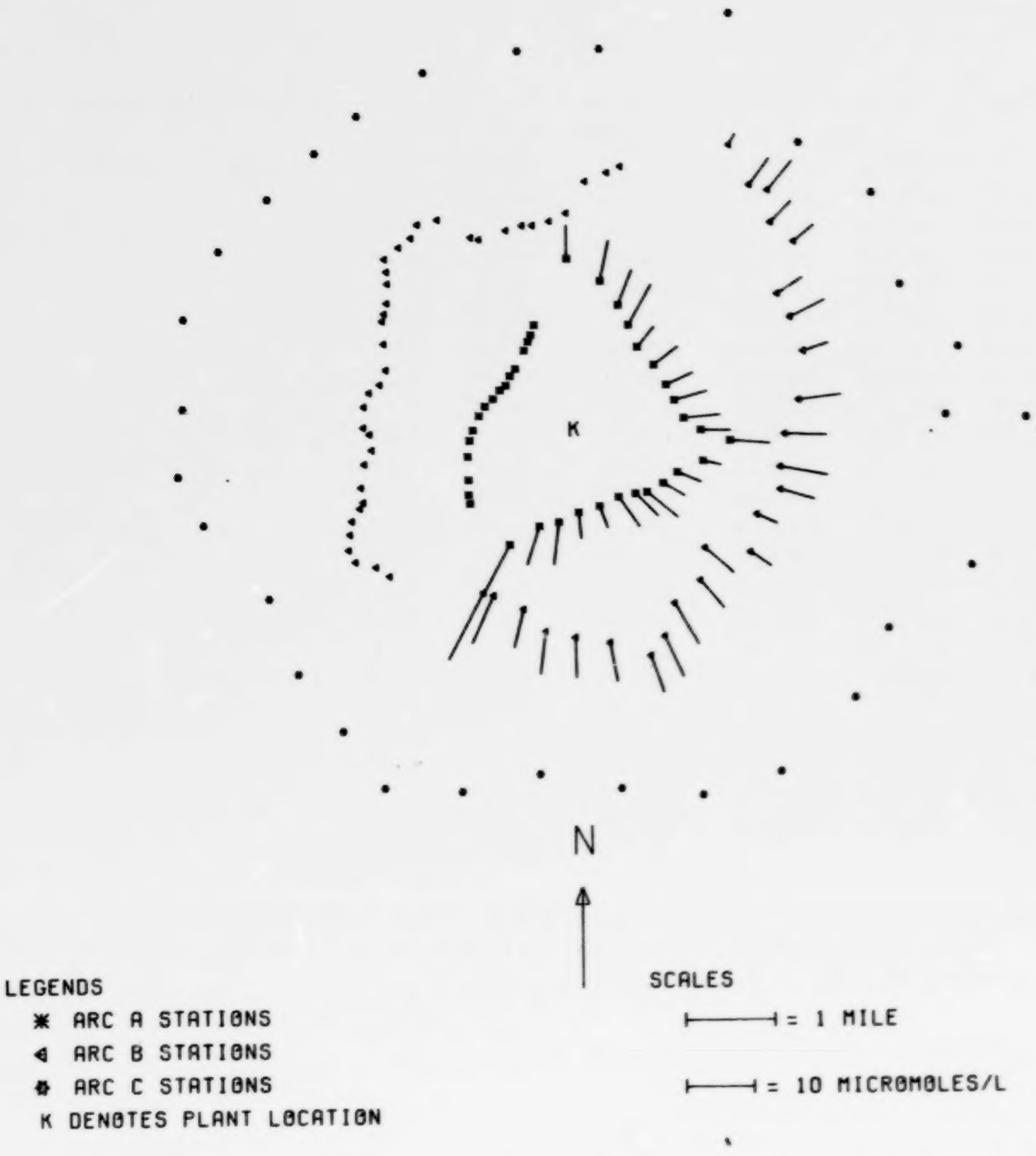

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
✲ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.22 Sulfur Dioxide Distribution, Run 11

TABLE A.23

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 11 FEB. 10, 1970 ARC A

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	12:54	14:49	73.0	6.9	3.4			
4.0	12:55	14:50	73.0	3.9	4.0			
6.0	12:57	14:52	76.0	4.5	3.4			
8.0	12:59	14:53	60.0	4.4	3.5			
10.0	13:00	14:55	75.0	5.0	4.6			
12.0	13:02	14:56	58.0	5.4	4.0			
14.0	13:03	14:58	63.0	4.4	5.4			
16.0	13:05	14:59	67.0	5.9	4.6			
18.0	12:50	14:44	64.0	2.7	6.9			
20.0	12:51	14:46	53.0	3.8	6.8			
22.0	12:53	14:48	80.0	3.7	4.0			
24.0	12:55	14:50	26.0	5.9	7.2			
26.0	12:57	14:52	63.0	4.8	4.4			
28.0	12:59	14:54	80.0	5.4	5.2			
30.0	13:01	14:56	80.0	3.4	5.0			
32.0	13:03	14:58	62.0	3.9	10.2			
34.0	13:05	15:00	67.0	6.4	3.7			
36.0	13:07	15:02	100.0	6.0	3.4			
38.0	13:09	15:04	65.0	7.8	4.6			
64.0	12:47	14:44	55.0	5.0	4.4			
66.0	12:50	14:46	93.0	6.2	4.3			
68.0	12:52	14:47	69.0	5.7	3.5			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.24

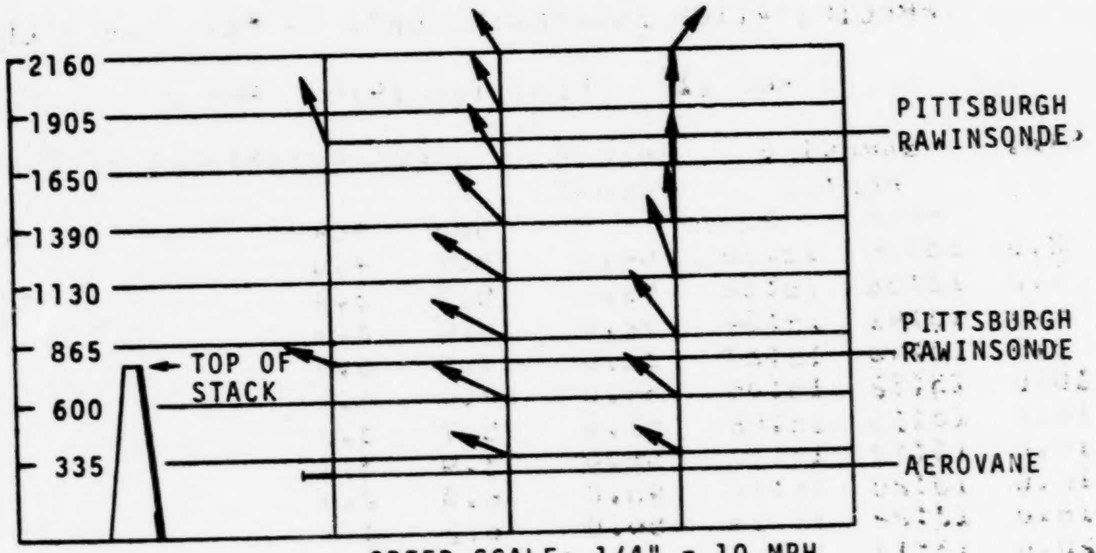
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 11 FEB. 10, 1970 ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
2.0	13:36	15:30	64.0	4.9	4.5			4.00
4.0	13:38	15:32	41.0	5.7	3.4			
6.0	13:41	15:34	52.0	4.4	3.4			3.90
8.0	13:43	15:37	32.0	3.8	3.5			
10.0	13:12	15:06	54.0	4.4	4.8			3.90
12.0	13:15	15:08	51.0	5.7	3.5			
14.0	13:17	15:10	56.0	3.9	3.4			4.00
16.0	13:20	15:12	43.0	6.3	2.4			3.90
18.0	13:22	15:14	56.0	6.2	3.2			3.70
20.0	13:17	15:16	69.0	7.1	3.5			
22.0	13:20	15:19	54.0	5.2	3.5			3.90
24.0	13:23	15:24	67.0	3.3	3.9			
26.0	13:27	15:27	51.0	3.8	3.7			4.00
28.0	13:29	15:30	59.0	5.7	4.0			
30.0	13:32	15:32	62.0	5.4	2.6			4.00
32.0	13:35	15:35	76.0	7.0	4.0			
34.0	13:38	15:37	36.0	6.7	3.0			4.15
36.0	13:40	15:40	86.0	5.8	2.8			
38.0	13:43	15:51	94.0	5.9	3.8			3.90
40.0	13:45	15:54	105.0	6.0	3.4			
42.0	13:48	15:57	124.0	6.4	3.5			3.90
44.0	13:51	16:00	143.0	5.8				
46.0	13:55	16:04	127.0	7.7	3.7			3.80
47.0	13:57	16:06	84.0	11.1	3.0			
94.0	13:33	15:27	44.0	1.9	3.0			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 12 DATE 2-14-70 TIME 2015-2124



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	1900	1725	2100	
2160	PIBAL		152/12	213/12	
1905	PIBAL		152/14	183/11	
1775	RAWIN	160/16			
1650	PIBAL		151/16	177/10	
1390	PIBAL		138/18	173/12	
1130	PIBAL		123/20	161/19	
865	PIBAL		118/20	146/19	
775	RAWIN	110/11			
600	PIBAL		115/19	130/16	
335	PIBAL		111/15	121/12	
300	AERO	090/4			

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.23 Wind Profiles, Run 12

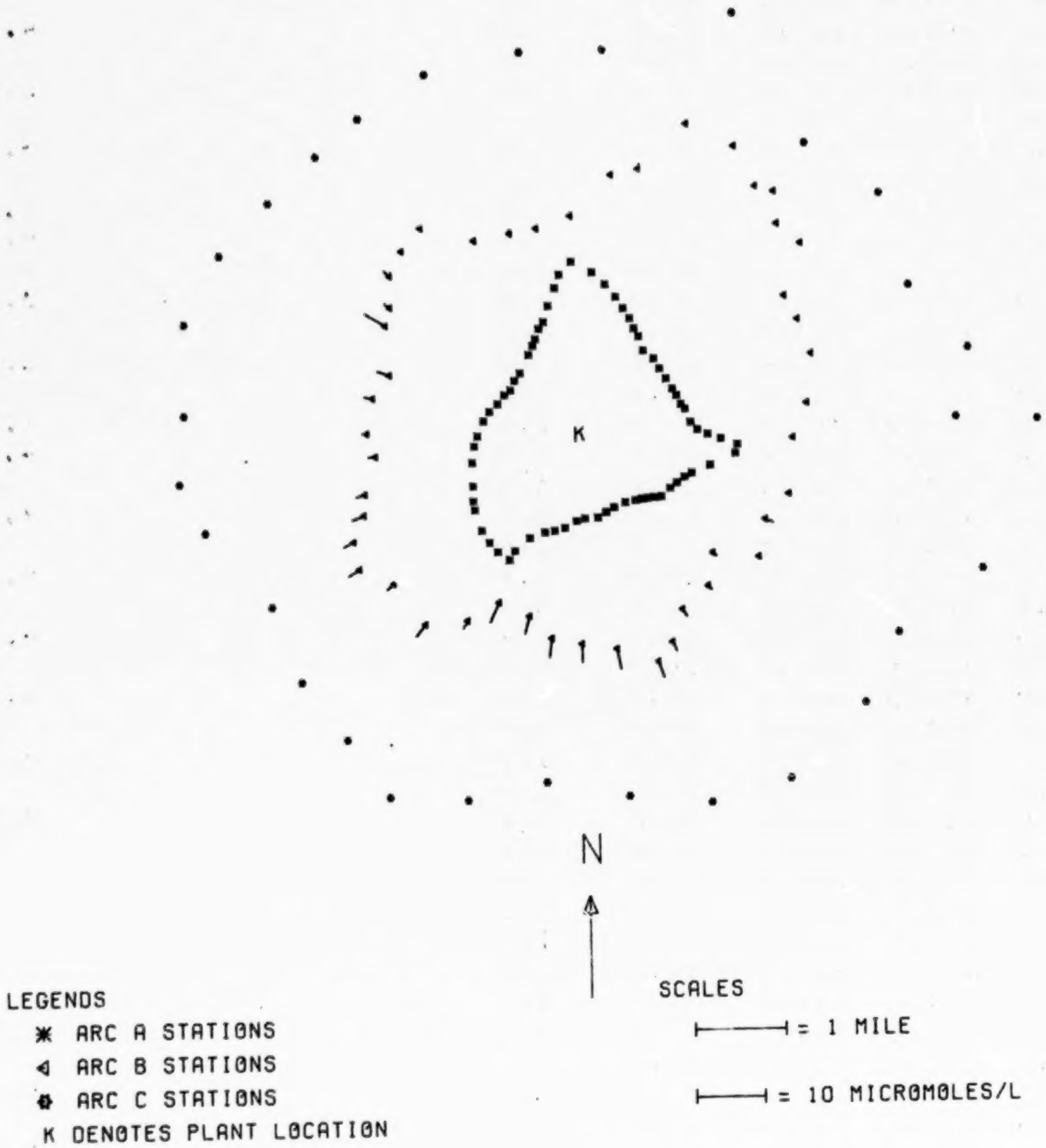

K
N
LEGENDS
✱ ARC A STATIONS
◄ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.24 Sulfur Dioxide Distribution, Run 12

TABLE A.25

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 12 FEB. 14, 1970 ARC B

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
2.0	20:07	22:10	24.0	.0				4.14
4.0	20:10	22:13	30.0	.2				
6.0	20:12	22:15	35.0	.2				4.18
8.0	20:15	22:17	57.0	.2				
10.0	18:46	21:30	22.0	.2				3.92
12.0	18:48	21:32	31.0	.1				
14.0	18:49	21:34	34.0	.2				3.78
16.0	18:50	21:36	33.0	.2				
18.0	18:52	21:39	25.0	.2				3.80
22.0	18:56	21:43	13.0	.2				4.22
24.0	19:07	21:47	17.0	1.4				4.22
26.0	19:09	21:50	38.0	.5				3.89
28.0	19:12	21:53	33.0	.8				
30.0	19:14	21:56	28.0	.8				3.89
32.0	19:16	21:59	34.0	1.3				
34.0	19:18	22:01	25.0	1.6				4.25
36.0	18:45	21:26	14.0	2.5				4.18
38.0	18:48	21:31	13.0	3.1				
40.0	18:50	21:32	18.0	2.7				4.22
42.0	18:52	21:35	21.0	2.9				
44.0	18:54	21:37	24.0	2.7				4.12
46.0	18:56	21:40	25.0	3.2				
48.0	18:59	21:44	18.0	1.4				4.85
50.0	19:01	21:47	10.0	2.2				
52.0	19:03	21:49	31.0	1.4				4.12
54.0	19:07	21:52	10.0	1.9				
56.0	19:08	21:55	37.0	1.7				3.98
58.0	19:10	21:57	10.0	1.9				
60.0	19:13	22:00	50.0	1.4				3.89
62.0	19:18	22:03	31.0	1.1				
64.0	19:20	22:05	18.0	.7				
66.0	19:24	22:08	26.0	1.3				
68.0	19:26	22:11	50.0	1.9				
70.0	19:05	21:24	24.0	3.5				
72.0	19:30	21:35	11.0	1.0				
74.0	19:39	21:40	32.0	1.1				3.90
76.0	19:42	21:44	28.0	.2				
78.0	19:44	21:46	32.0	.3				4.02
80.0	19:47	21:49	29.0	.5				
82.0	19:48	21:51	28.0	.4				4.03
84.0	19:50	21:53	39.0	.2				
86.0	19:54	21:55	22.0	.2				3.93
88.0	19:55	21:59	27.0	.0				
90.0	19:57	22:00	18.0	.8				4.24
92.0	20:01	22:04	28.0	.5				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.26

SUMMARY OF FIELD PERIOD III -- APRIL-MAY, 1970

Date	Run No.	Wind[1] Velocity (deg/mph)	SO_2 Emission (tons-hr^{-1})	Arcs	Run Time[2]	Sampling[3] Duration (min)	Precip.[4] Rate (mm-hr^{-1})	SO_2 Recovery (μmoles)	SO_2 Concentration Max	Mean	Min
									(μmoles-liter^{-1})		
4-13	13	151/4	12.3	B	1435-1632	158	0.004	3.10	33.8	21.0	1.7
4-14	14	095/8	11.7	B	0923-1029	102	0.66	149.65	21.2	17.1	13.3
4-14	15	090/8	11.7	B	1107-1225	132	1.03	95.10	20.9	13.6	10.0
4-19	16	110/10	10.9	C	1349-1640	209	0.04	4.89	27.8	15.6	0.3
4-23	17	218/18	23.3	C	1025-1521	327	Dry				
4-24	18	234/12	19.5	C	0912-0958	81	1.00	2.00	1.7	0.5	0.2
4-24	19	235/10	18.1	C	1038-1443	286	0.19	7.04	8.7	2.7	0.3
4-24	20	325/18[5]	18.0	C	1554-1630	100	1.44	58.20	29.1	8.8	4.7
4-29	21	270/11[6]	12.4	A B	1048-1440 1115-1445	255 255	Dry				
5-2	22	315/9[7]	24.1	B	1518-1833	215	0.35	3.46	0.6	0.3	0.2

---

[1] Wind velocity at stack exit, unless otherwise noted

[2] Time of concurrent sampling by all collectors.

[3] Average duration of collector exposure

[4] Average rate determined from average volume of precipitation collected and average duration of collector exposure.

[5] 1900 EST Pittsburgh rawinsonde.

[6] 0700 EST Pittsburgh rawinsonde.

[7] 1900 EST Pittsburgh rawinsonde.

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TABLE A.27

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 13 APRIL 13, 1970 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	13:44	17:13	12.5	21.9				
4.0	14:13	16:38	.5	11.5				
6.0	14:15	16:41	1.5	5.3				
8.0	14:16	16:43	1.5	17.7				
10.0	14:18	16:47	2.5	9.9				
12.0	14:19	16:49	1.5	38.9				
14.0	14:20	16:51	5.5	22.7				
16.0	14:22	16:54	10.0	25.2				
18.0	14:23	16:56	2.0	83.8				
20.0	14:24	16:57	6.5	17.5				
22.0	14:25	16:59	11.0	21.9				
24.0	14:27	17:02	3.5	21.2				
26.0	14:28	17:04	1.5	30.2				
28.0	14:30	17:06	8.5	30.2				
30.0	14:31	17:08	1.5	26.5				
32.0	14:32	17:10	3.5	28.5				
34.0	14:33	17:13	2.5	29.7				
36.0	14:34	17:14	1.5	11.6				
38.0	14:35	17:16	9.5	19.3				
54.0	13:51	16:32	1.5	77.7				
56.0	13:52	16:34	1.5	1.7				
58.0	13:54	16:35	1.0	2.6				
60.0	13:55	16:37	1.0	20.8				
62.0	13:56	16:39	1.5	5.3				
64.0	13:57	16:40	1.5	8.9				
66.0	13:58	16:42	1.0	18.2				
68.0	14:00	16:43	1.0	.0				
70.0	14:01	16:45	1.5	3.5				
72.0	14:04	16:46	3.5	23.6				
74.0	14:05	16:48	16.5	35.5				
76.0	14:07	16:50	15.0	26.4				
78.0	14:08	16:51	14.0	17.6				
80.0	14:10	16:53	1.5	7.1				
82.0	14:12	16:55	1.5	24.8				
84.0	14:13	16:57	2.5	26.4				
86.0	14:15	16:59	.5	25.5				
88.0	14:17	17:02	.5	20.2				
90.0	14:18	17:03	.5	10.2				
92.0	14:21	17:05	1.5	8.8				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

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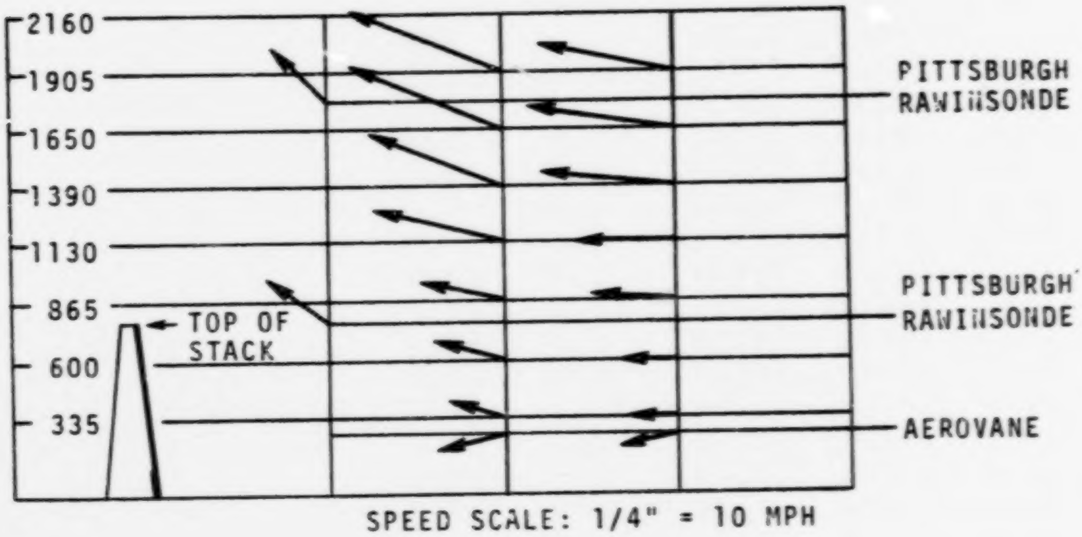
RUN NO. 14 DATE 4-14-70 TIME 0923-1029



HEIGHT (FT)	TIME →	0700	0910	1040	
2160	PIBAL				
1905	PIBAL		110/36	101/32	
1775	RAWIN	135/17			
1650	PIBAL		111/36	098/24	
1390	PIBAL		110/32	094/32	
1130	PIBAL		103/30	090/23	
865	PIBAL		101/19	090/20	
775	RAWIN	125/17			
600	PIBAL		107/16	090/13	
335	PIBAL		105/14	090/12	
300	AERO		080/15	080/14	

NOTES: 1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.

2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.

3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.

4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.25 Wind Profiles, Run 14

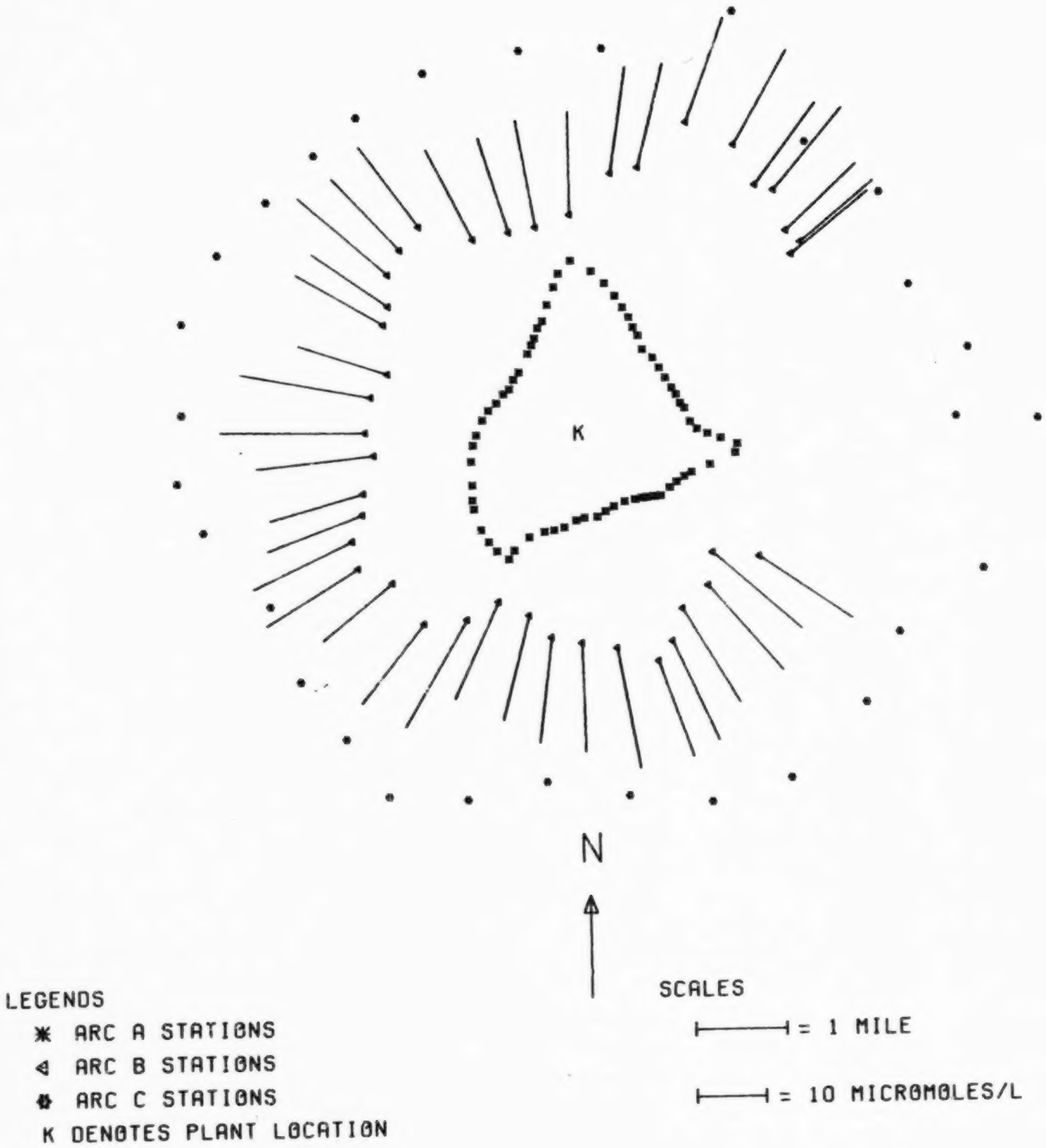


Figure A.26 Sulfur Dioxide Distribution, Run 14

TABLE A.28

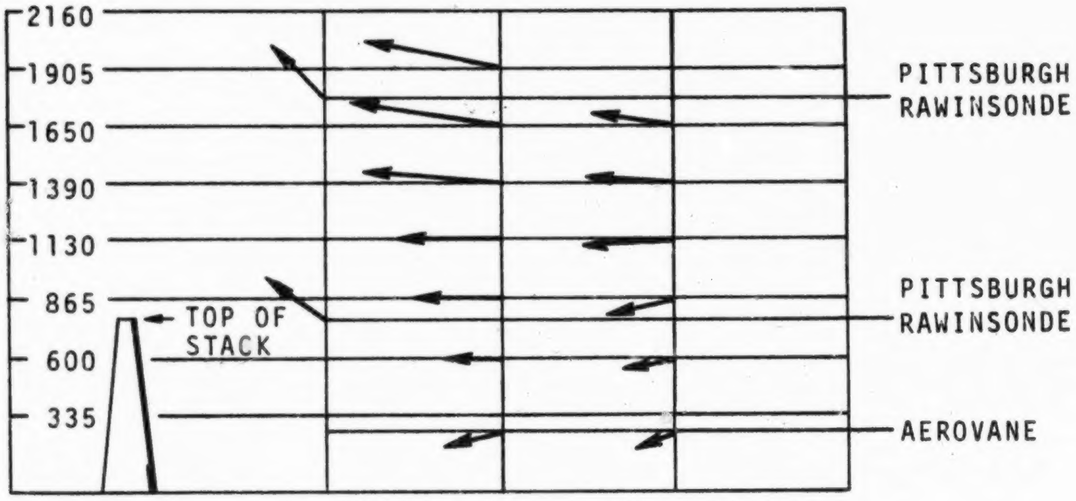
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 14 APRIL 14, 1976 ARC B

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	8:55	10:45	266.0	16.2				
2.0	9:30	13:45	237.0	15.0				
4.0	9:33	13:48	236.0	15.8				
7.0	9:36	13:50	246.0	14.2				
8.0	9:38	13:52	234.0	14.0				
9.0	9:39	13:56	240.0	14.6	7.5			
26.0	8:51	10:29	240.0	16.3	5.9			
28.0	8:53	10:32	259.0	17.2				
30.0	8:54	10:34	261.0	16.6				
32.0	8:56	10:35	246.0	16.2				
34.0	8:57	10:37	236.0	16.1				
36.0	8:58	10:39	174.0	15.0				
38.0	8:59	10:41	247.0	18.1				
40.0	9:00	10:44	259.0	16.1				
42.0	9:02	10:45	246.0	15.7				
44.0	9:03	10:47	240.0	15.9				
46.0	9:04	10:49	206.0	15.7				
48.0	9:06	10:52	206.0	18.2				
50.0	9:08	10:54	244.0	14.9				
52.0	9:10	10:56	193.0	13.3				
54.0	9:16	10:58	192.0	15.8				
56.0	9:17	11:00	193.0	16.1				
58.0	9:18	11:02	210.0	14.9	8.3			
60.0	9:20	11:05	225.0	14.2	5.7			
62.0	9:21	11:07	215.0	17.3	6.8			
64.0	9:23	11:10	245.0	21.2	4.2			
66.0	8:54	10:32	260.0	19.4	6.3			
68.0	8:55	10:34	265.0	13.8	3.7			
70.0	8:57	10:36	265.0	14.9	5.2			
72.0	8:58	10:38	265.0	13.6	4.0			
74.0	9:00	10:40	260.0	17.4				
76.0	9:01	10:42	264.0	14.5				
78.0	9:03	10:43	262.0	14.8				
80.0	9:04	10:45	260.0	15.0				
82.0	9:06	10:47	263.0	14.7				
84.0	9:08	10:49	263.0	16.1				
86.0	9:10	10:51	260.0	15.3				
88.0	9:12	10:53	260.0	16.0				
90.0	9:13	10:55	262.0	15.9				
92.0	9:15	10:57	262.0	16.4				
94.0	9:16	11:00	263.0	16.2				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 15 DATE 4-14-70 TIME 1107-1225



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	1040	1140	
2160	PIBAL				
1905	PIBAL		101/32		
1775	RAWIN	135/17			
1650	PIBAL		098/24	098/19	
1390	PIBAL		094/32	093/20	
1130	PIBAL		090/23	087/20	
865	PIBAL		090/13	080/14	
775	RAWIN	125/17			
600	PIBAL		090/12	079/16	
335	PIBAL				
300	AERO		080/14	065/10	

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.27 Wind Profiles, Run 15

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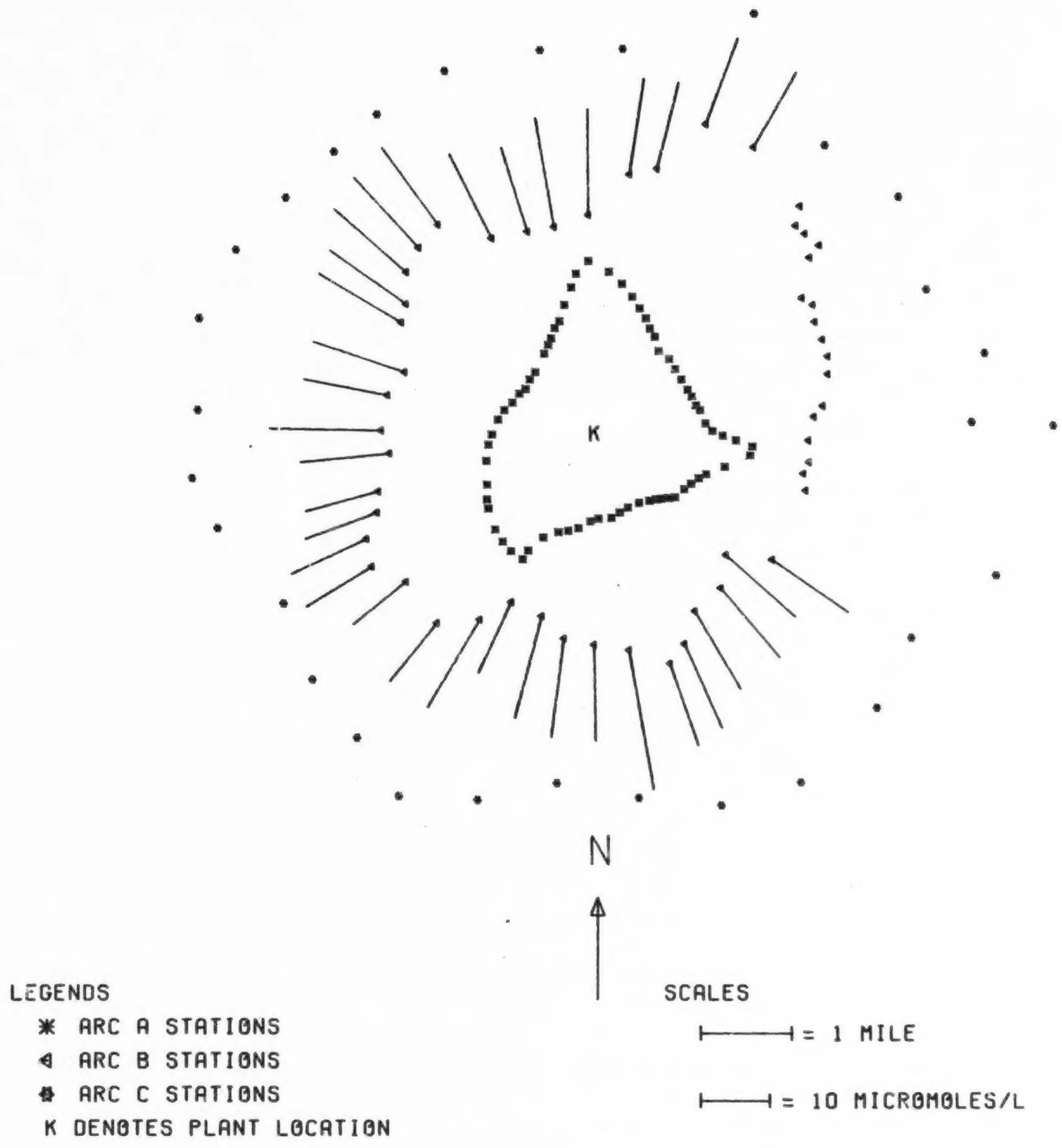

K
N
LEGENDS
✱ ARC A STATIONS
◄ ARC B STATIONS
✱ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.28 Sulfur Dioxide Distribution, Run 15

TABLE A.29

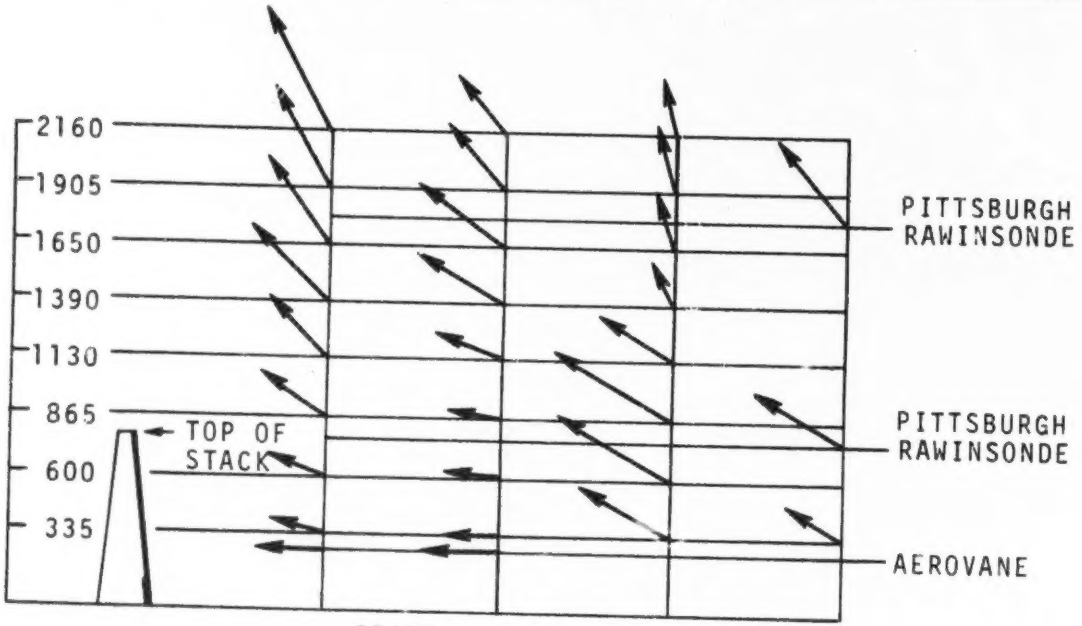
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 15 APRIL 14, 1970 ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
.0	10:45	12:25	154.0	16.2				
26.0	10:29	12:35	240.0	13.5	7.0			
28.0	10:32	12:36	244.0	13.6				
30.0	10:34	12:38	255.0	13.3				
32.0	10:35	12:40	200.0	13.3				
34.0	10:37	12:43	219.0	13.6				
36.0	10:39	12:44	144.0	12.8				
38.0	10:41	12:46	167.0	20.9				
40.0	10:44	12:47	157.0	14.2				
42.0	10:45	12:49	145.0	14.7				
44.0	10:47	12:50	141.0	15.5				
46.0	10:49	12:53	131.0	11.5				
48.0	10:52	12:55	136.0	15.0				
50.0	10:54	12:57	197.0	11.0				
52.0	10:56	12:59	166.0	10.0				
54.0	10:58	13:01	195.0	11.2				
56.0	11:00	13:03	196.0	12.1				
58.0	11:02	13:05	210.0	11.2	5.9			
60.0	11:05	13:07	185.0	11.0	6.1			
62.0	11:07	13:10	205.0	13.1	9.9			
64.0	11:10	13:13	225.0	16.3	6.8			
66.0	10:32	12:51	225.0	12.4	6.2			
68.0	10:34	12:54	235.0	14.1	4.3			
70.0	10:36	12:56	190.0	14.1	3.3			
72.0	10:38	12:59	210.0	13.7	4.6			
74.0	10:40	13:01	202.0	14.1				
76.0	10:42	13:03	222.0	14.1				
78.0	10:43	13:05	228.0	14.1				
80.0	10:45	13:07	234.0	14.0				
82.0	10:47	13:10	266.0	13.0				
84.0	10:49	13:12	247.0	16.4				
86.0	10:51	13:15	82.0	15.7				
88.0	10:53	13:17	212.0	14.3				
90.0	10:55	13:19	241.0	13.2				
92.0	10:57	13:21	16.0	13.5				
94.0	11:00	13:26	245.0	12.7	5.0			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATIO UNITS ARE MILLIGRAMS/L.

RUN NO. 16 DATE 4-19-70 TIME 1349-1640



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	1200	1348	1627	1900
2160	PIBAL	152/31	139/17	168/12	
1905	PIBAL	150/27	139/21	165/15	
1775	RAWIN				140/26
1650	PIBAL	144/25	127/25	162/14	
1390	PIBAL	135/24	121/23	152/10	
1130	PIBAL	127/19	113/17	121/20	
865	PIBAL	113/18	100/13	119/33	
775	RAWIN				120/24
600	PIBAL	110/15	096/12	119/31	
335	PIBAL	101/12	090/10	121/25	120/14
300	AERO	090/15	090/16		

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.29 Wind Profiles, Run 16

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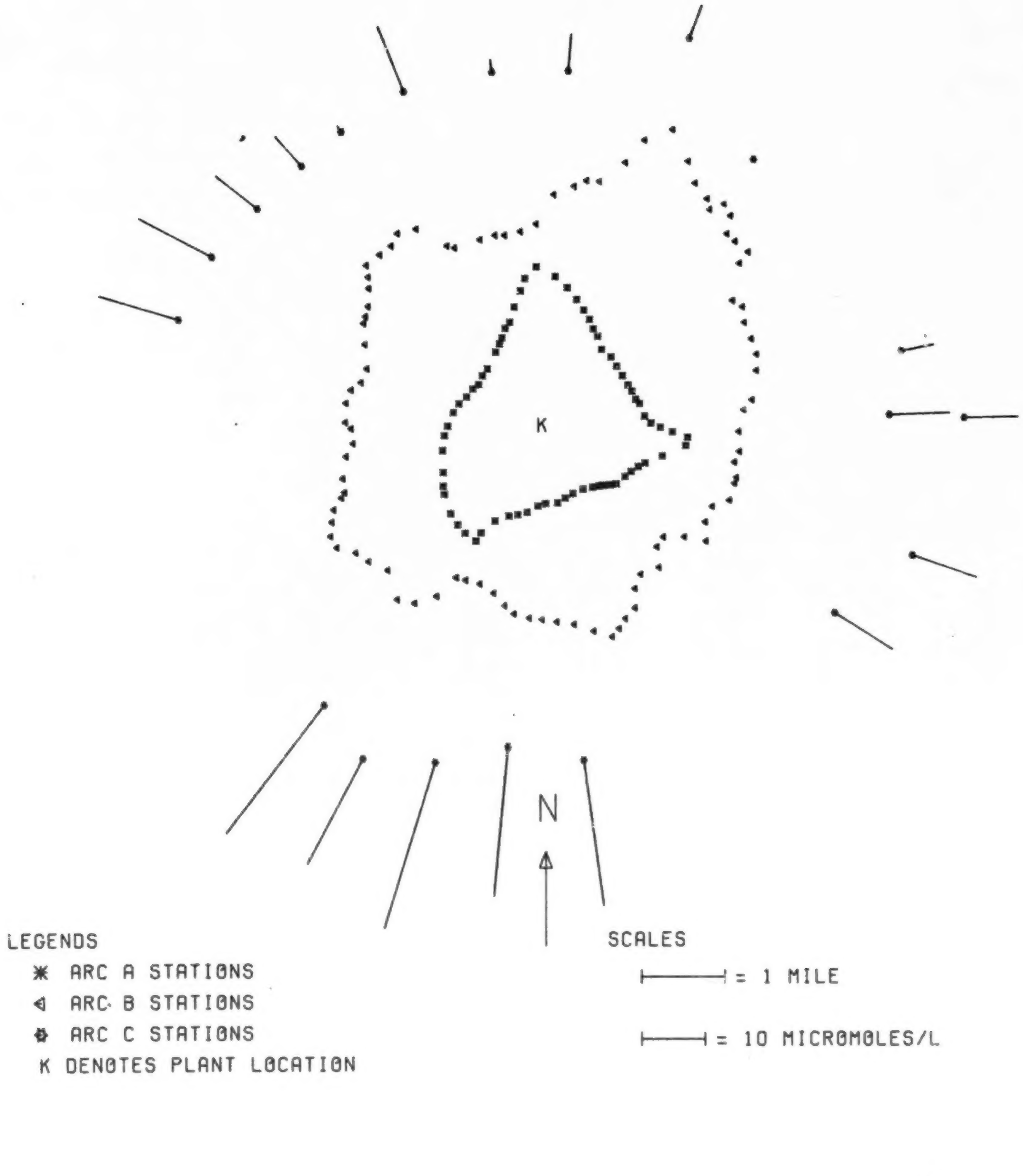

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
✱ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
⊢——⊣ = 1 MILE
⊢——⊣ = 10 MICROMOLES/L

Figure A.30 Sulfur Dioxide Distribution, Run 16

TABLE A.30

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 16 APRIL 19, 1970 ARC C

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
1.0	13:32	17:03	17.0	.3				
4.0	13:16	16:43	29.0	5.3				
5.0	13:19	16:46	26.5	9.5				
6.0	13:25	16:52	25.5	8.5				
7.0	13:30	16:59	15.0	10.7				
8.0	13:35	17:05	5.0	10.6				
12.0	13:15	16:40	31.0	23.6				
13.0	13:19	16:45	24.0	24.1				
14.0	13:22	16:49	19.5	27.8				
15.0	13:25	16:53	5.0	19.0				
16.0	13:28	16:57	6.0	25.8				
22.0	13:20	16:42	20.0	13.6				
23.0	13:25	16:52	23.0	13.8				
23.5	13:28	16:54	23.0	10.6				
24.0	13:29	16:58	16.0	8.4				
24.5	13:31	17:00	11.5	7.0				
25.0	13:36	17:04	5.5	6.3				
26.0	13:41	17:07	2.0	1.1				
27.0	13:46	17:16	11.0	11.1				
28.5	13:43	17:10	3.0	14.0				
28.0	13:16	16:43	31.5	2.0				
29.0	13:19	16:48	32.0	5.9				
29.5	13:22	16:52	26.0	7.8				
30.0	13:26	16:57	21.0	5.6				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.31

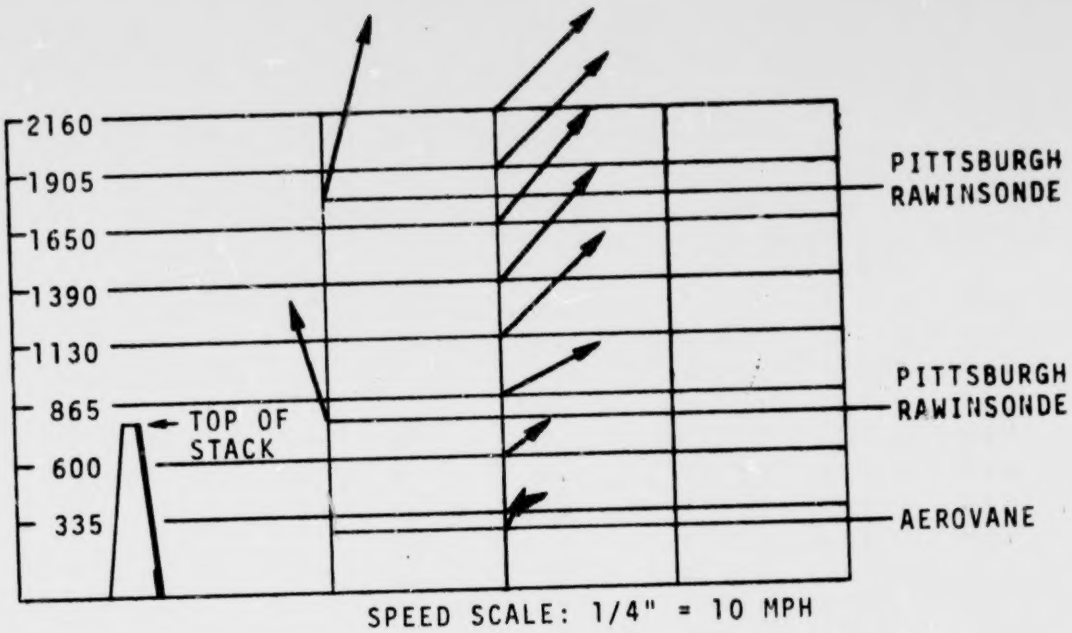
PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 17 APRIL 23, 1970 ARC C

STA.	SAMPLING PERIOD FROM	SAMPLING PERIOD TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
1.0	10:10	15:35	.0	.4				
1.5	10:12	15:38	.0	.5				
2.0	10:16	15:42	.0	1.7				
3.0	10:21	15:48	.0	.6				
4.0	10:00	15:24	.0	.8				
5.0	10:01	15:26	.0	.0				
6.0	10:07	15:32	.0	.0				
7.0	10:13	15:38	.0	.0				
10.0	10:23	15:52	.0	.2				
12.0	10:00	15:21	.0	.0				
14.0	10:07	15:29	.0	.2				
15.0	10:09	15:33	.0	.5				
16.0	10:11	15:38	.0	.0				
18.0	10:17	15:45	.0	.0				
20.0	10:23	15:54	.0	1.1				
21.0	10:25	15:56	.0	.0				
22.0	10:00	15:25	.0	.4				
23.0	10:05	15:34	.0	.4				
24.0	10:08	15:37	.0	2.2				
25.0	10:10	15:39	.0	.8				
26.0	10:14	15:43	.0	.0				
27.0	10:17	15:47	.0	.0				
28.0	10:25	15:55	.0	1.6				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 18 DATE 4-24-70 TIME 0912-0958



SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	1002		
2160	PIBAL		225/32		
1905	PIBAL		225/38		
1775	RAWIN	195/44			
1650	PIBAL		220/34		
1390	PIBAL		222/36		
1130	PIBAL		226/34		
865	PIBAL		234/26		
775	RAWIN	165/29			
600	PIBAL		238/16		
335	PIBAL		246/11		
300	AERO		210/10		

NOTES: 1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.

2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.

3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.

4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.31 Wind Profiles, Run 18

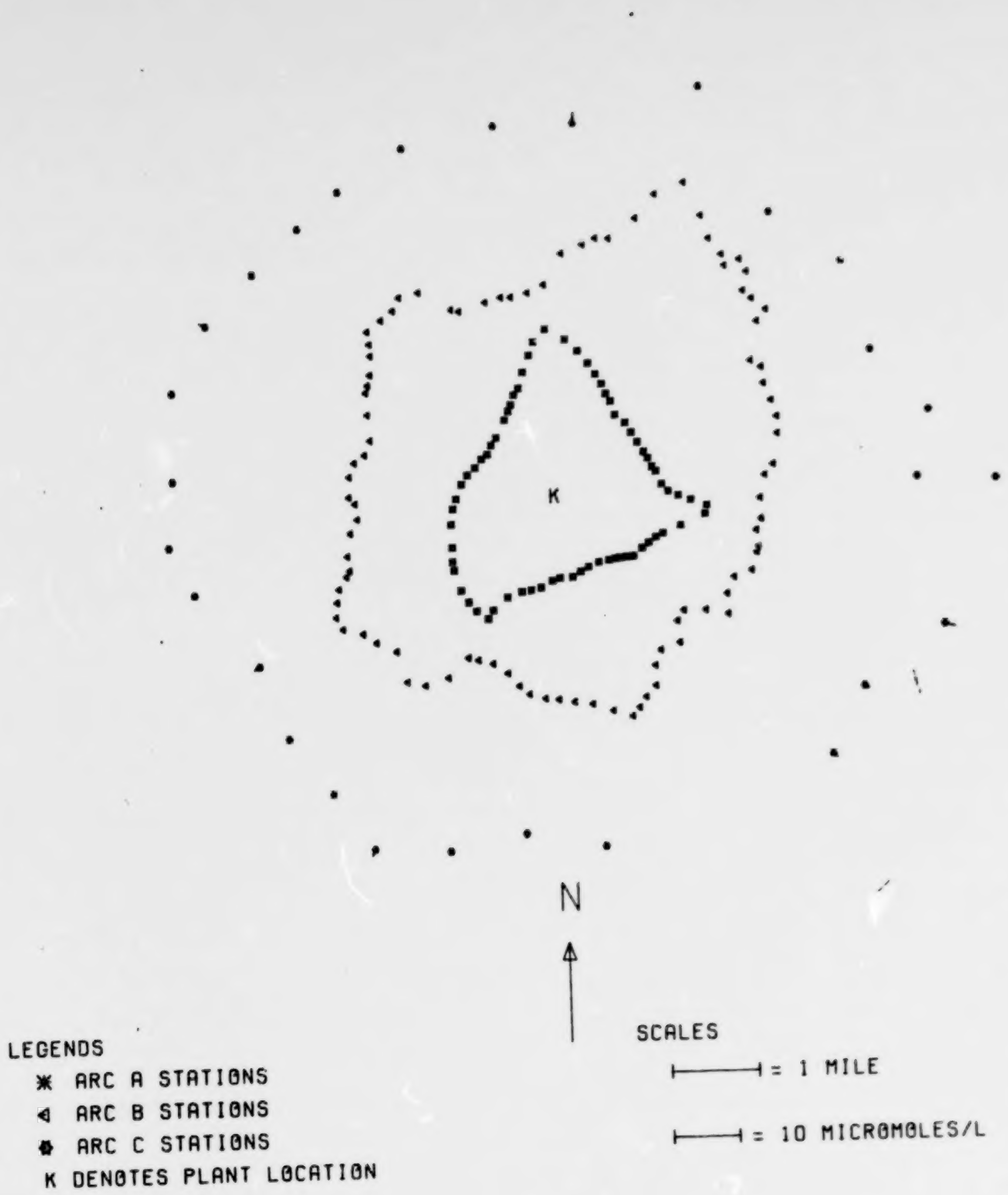

K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.32 Sulfur Dioxide Distribution, Run 18

TABLE A.32

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 18 APRIL 24, 1970 ARC A

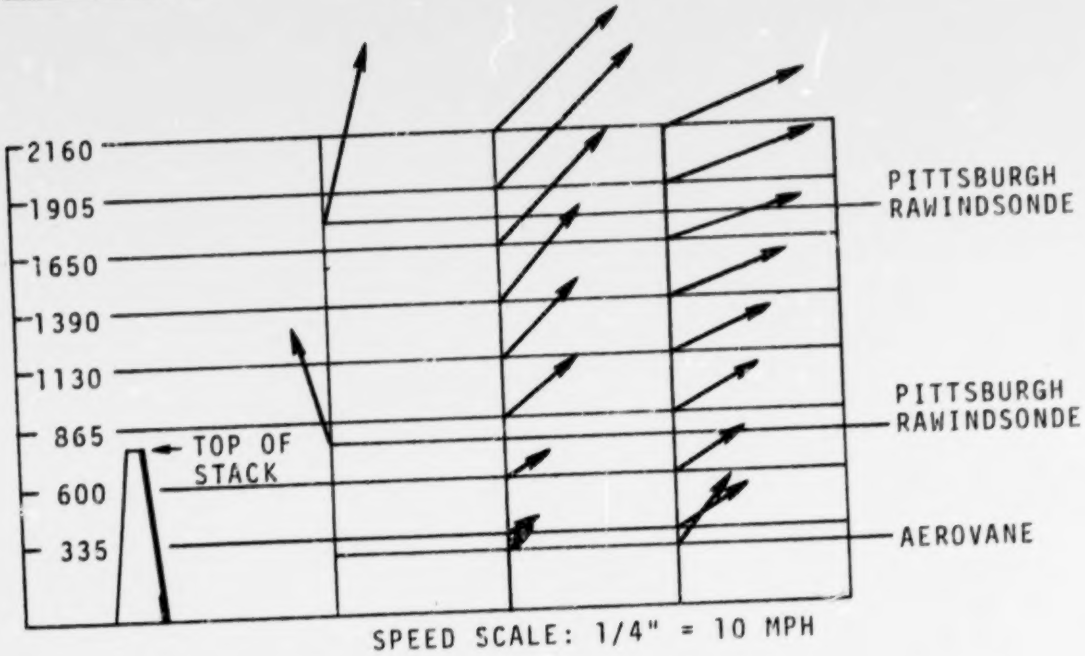
STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
3.0	8:59	10:19	82.0	.3				
6.0	9:02	10:22	2.0	.9				

RUN 18 APRIL 24, 1970 ARC C

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	8:45	10:05	92.0	.3		.0540	3.95	3.80
1.0	9:02	10:24	122.0	.3	16.5	.0270	4.26	3.72
2.0	9:08	10:31	102.0	.3				
3.0	9:12	10:38	93.0	.3				
4.0	8:43	9:58	87.0	.6	12.7	.0470	5.08	4.00
5.0	8:45	10:03	47.0	.4				
6.0	8:51	10:09	29.0	.6	13.4			
7.0	8:58	10:15	14.0	1.7	25.0	.0670		
8.0	9:03	10:23	10.0	.8	15.5			
9.0	9:06	10:26	2.0	.9				
12.0	8:41	10:00	10.0	.2	14.8			
13.0	8:45	10:03	13.0	.7	13.1			
14.0	8:47	10:07	7.0	.5		.0870		
15.0	8:49	10:13	6.0	1.1				
16.0	8:53	10:17	67.0	.3				
17.0	8:57	10:21	37.0	.4				
18.0	9:00	10:27	35.0	1.0	11.0	.0500	4.60	3.92
19.0	9:03	10:32	97.0	.3				
20.0	9:05	10:35	217.0	.3				
21.0	8:45	10:00	237.0	.3				
22.0	8:49	10:06	190.0	.4	11.6	.0300	3.60	3.93
23.0	8:53	10:10	177.0	1.1	13.5			
24.0	8:55	10:14	192.0	.3				
25.0	8:58	10:19	213.0	.3	11.0	.0300	3.44	4.00
26.0	9:00	10:24	212.0	.4				
27.0	9:04	10:28	212.0	.3				
27.5	9:09	10:31	262.0	.3	8.0	.0250	2.66	4.05
28.0	8:45	10:00	217.0	.4				
29.0	8:48	10:04	262.0	1.6	9.7			
29.5	8:52	10:10	262.0	.6	8.9	.0170	3.18	4.02
30.0	8:55	10:15	262.0	.6	10.8			
30.5	8:58	10:19	197.0	.3				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

RUN NO. 19 DATE 4-24-70 TIME 1038-1443



HEIGHT (FT)	TIME →	0700	1105	1405	
2160	PIBAL		226/40	249/36	
1905	PIBAL		225/46	251/38	
1775	RAWIN	195/44			
1650	PIBAL		225/37	254/34	
1390	PIBAL		221/29	251/30	
1130	PIBAL		224/25	246/26	
865	PIBAL		230/23	242/23	
775	RAWIN	165/29			
600	PIBAL		238/12	239/20	
335	PIBAL		244/18	238/21	
300	AERO		230/8	220/20	

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.33 Wind Profiles, Run 19

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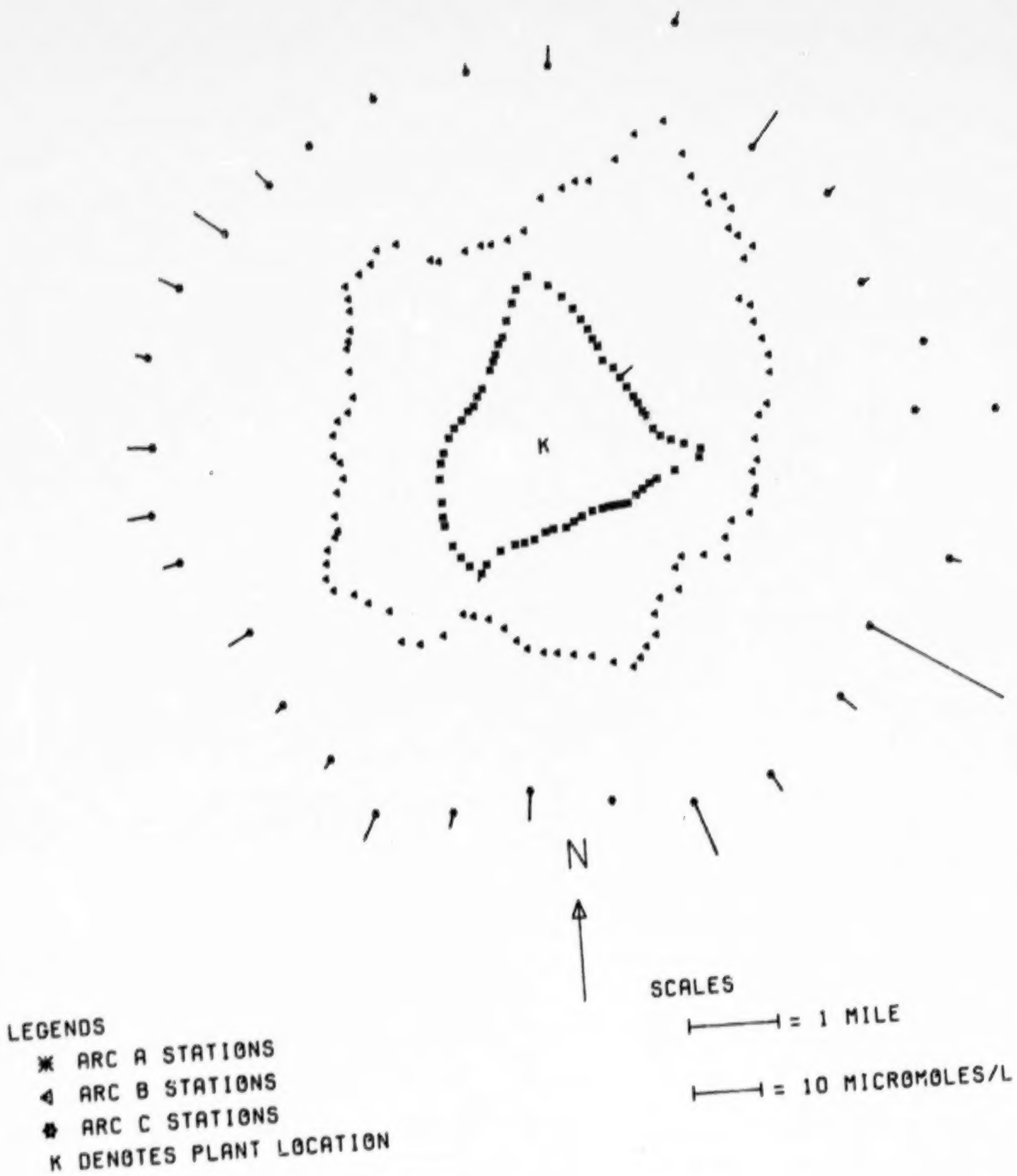
K
N
SCALES
= 1 MILE
= 10 MICROMOLES/L
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION

Figure A.34 Sulfur Dioxide Distribution, Run 19

TABLE A.33

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 19 APRIL 24, 1970 ARC A

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
3.0	10:20	14:52	72.0	.8				
6.0	10:23	14:55	72.0	2.5				
39.0	10:11	14:44	42.0	1.3				

RUN 19 APRIL 24, 1970 ARC C

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
.0	10:05	14:45	37.0	.9		.0210		3.75
1.0	10:24	15:06	229.0	6.5		.0100	2.58	3.94
2.0	10:31	15:12	102.0	1.4		.0140		4.08
3.0	10:38	15:17	97.0	1.3		.0150		4.00
4.0	9:58	14:43	65.0	.6		.0280	4.90	4.06
5.0	10:03	14:47	42.0	.7				
6.0	10:09	14:53	32.0	.3	15.6			
7.0	10:15	15:00	25.0	1.8	16.1			
8.0	10:23	15:35	13.0	22.4				
9.0	10:26	15:43	47.0	3.1	16.9			
10.0	10:31	15:50	37.0	3.0		.0280		4.23
11.0	10:34	15:54	50.0	8.7				
12.0	10:00	14:45	32.0	.7				
13.0	10:03	14:53	32.0	4.5				
14.0	10:07	14:58	17.0	2.4		.0370	8.52	4.20
15.0	10:13	15:02	42.0	4.4				
16.0	10:17	15:05	67.0	1.6				
17.0	10:21	15:10	71.0	1.5				
18.0	10:27	15:15	117.0	3.7		.0200	4.33	4.01
19.0	10:32	15:20	142.0	2.6				
20.0	10:35	15:24	147.0	3.6				
21.0	10:00	14:45	112.0	3.7				
22.0	10:06	14:48	97.0	1.9		.0150	3.12	4.13
23.0	10:10	14:53	82.0	3.4	9.9			
24.0	10:14	14:55	27.0	5.6				
25.0	10:19	15:00	54.0	2.9		.0320	5.42	4.13
26.0	10:24	15:04	47.0	.5				
27.0	10:28	15:07	65.0	.9				
27.5	10:31	15:15	177.0	1.8		.0180	2.65	4.18
28.0	10:00	14:45	42.0	1.2	9.1			
29.0	10:04	14:48	172.0	2.9				
29.5	10:10	14:53	102.0	1.1		.0210	4.34	4.00
30.0	10:15	14:58	67.0	1.7				
30.5	10:19	15:01	102.0	.3	11.1			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

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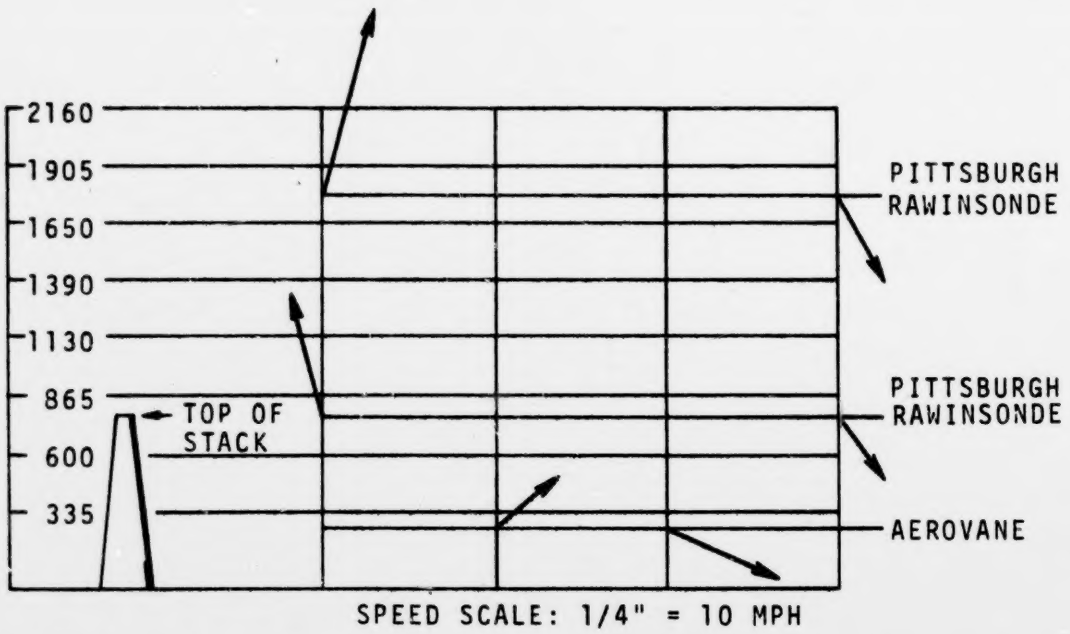
RUN NO. 20 DATE 5-24-70 TIME 1554-1630


2160
1905
1650
1390
1130
865
600
335
TOP OF STACK
PITTSBURGH RAWINSONDE
PITTSBURGH RAWINSONDE
AEROVANE
SPEED SCALE: 1/4" = 10 MPH

HEIGHT (FT)	TIME →	0700	1545	1615	1900
2160	PIBAL				
1905	PIBAL				
1775	RAWIN	195/44			330/23
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN	165/29			325/18
600	PIBAL				
335	PIBAL				
300	AERO		230/19	290/30	

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.35 Wind Profiles, Run 20

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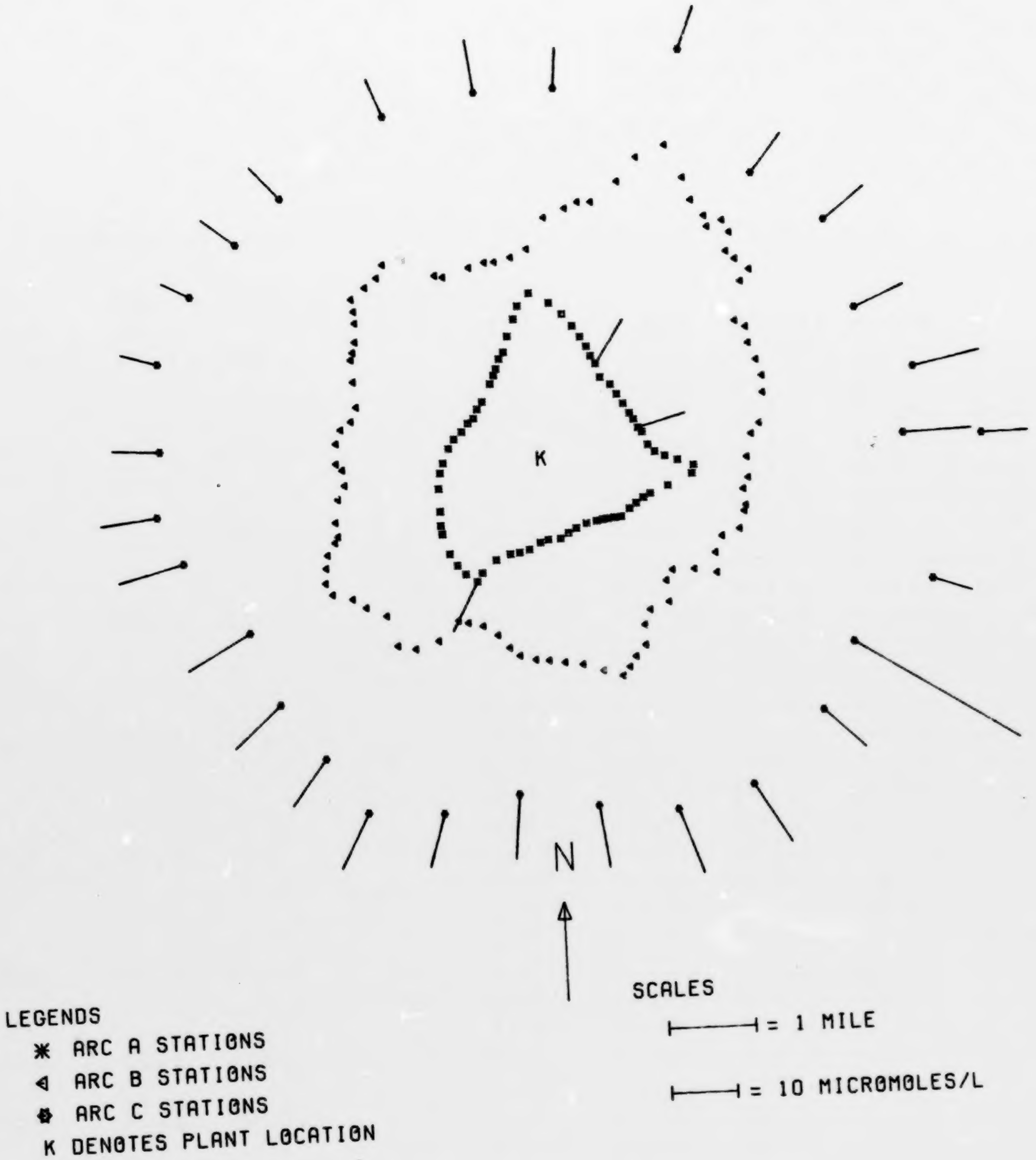
K
N
LEGENDS
✱ ARC A STATIONS
◁ ARC B STATIONS
⬢ ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.36 Sulfur Dioxide Distribution, Run 20

TABLE A.34

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 20 APRIL 24, 1970 ARC A

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
3.0	14:52	16:38	217.0	7.9				
10.0	14:58	16:41	163.0	7.5				
39.0	14:44	16:30	247.0	8.5				

RUN 20 APRIL 24, 1970 ARC C

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
.0	14:45	16:35	77.0	9.8			2.35	4.23
1.0	15:06	16:54	265.0	7.6		.0190	1.27	4.39
2.0	15:12	17:02	258.0	7.9				
3.0	15:17	17:07	127.0	8.2				
4.0	14:43	16:30	222.0	10.3		.0200	2.35	4.05
5.0	14:47	16:32	221.0	10.3				
6.0	14:53	16:37	212.0	7.0				
7.0	15:00	16:44	232.0	6.2		.0230		4.22
8.0	15:35	16:49	177.0	29.1	6.3			
9.0	15:43	16:53	197.0	8.6	4.7			
10.0	15:50	16:58	167.0	10.7		.0230	1.78	4.30
11.0	15:54	17:00	132.0	10.6	6.6			
12.0	14:45	16:30	167.0	9.7	6.0			
13.0	14:53	16:34	132.0	10.0				
14.0	14:58	16:37	173.0	8.5		.0200	1.92	4.31
15.0	15:02	16:40	223.0	9.5				
16.0	15:05	16:43	254.0	8.8				
17.0	15:10	16:46	262.0	9.6				
18.0	15:15	16:50	212.0	11.0		.0140	2.00	4.41
19.0	15:20	16:54	200.0	10.2				
20.0	15:24	16:58	219.0	8.6				
21.0	14:45	16:30	262.0	7.2				
22.0	14:48	16:35	217.0	5.8		.0100	1.86	4.27
23.0	14:53	16:40	247.0	4.8	8.0			
24.0	14:55	16:45	62.0	6.5				
25.0	15:00	16:50	262.0	6.7		.0110	1.35	4.40
27.0	15:07	17:00	270.0	6.3				
27.5	15:15	17:08	262.0	6.4		.0100	1.32	4.44
28.0	14:45	16:30	273.0	8.2	6.7			
29.0	14:48	16:33	207.0	6.2				
29.5	14:53	16:38	262.0	8.1		.0150	2.19	4.20
30.0	14:58	16:45	122.0	7.0				
30.5	15:01	16:49	222.0	4.7	6.9			

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

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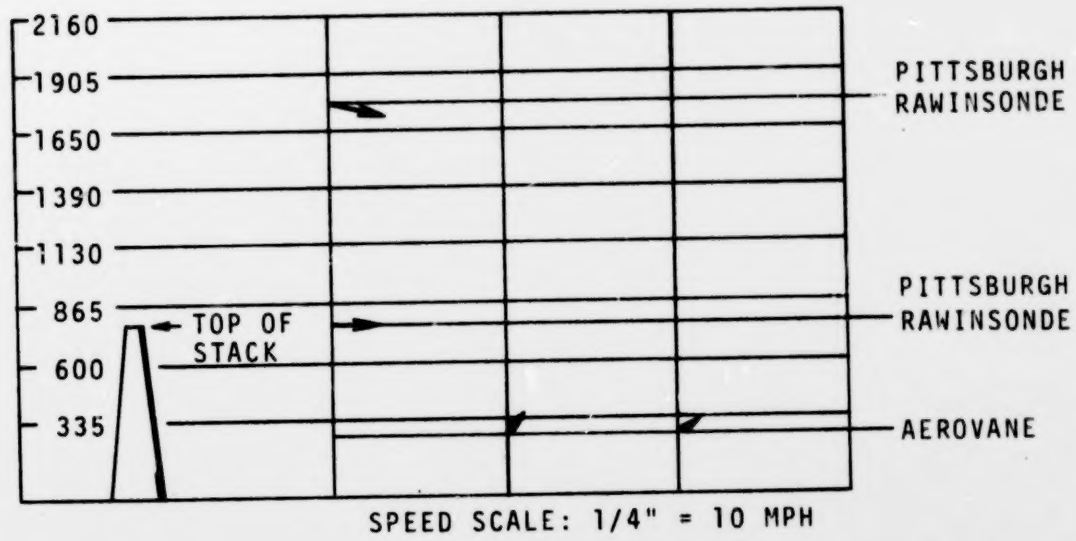
RUN NO. 21 DATE 4-29-70 TIME 1048-1445



HEIGHT (FT)	TIME →	0700	1100	1300	
2160	PIBAL				
1905	PIBAL				
1775	RAWIN	280/14			
1650	PIBAL				
1390	PIBAL				
1130	PIBAL				
865	PIBAL				
775	RAWIN	270/11			
600	PIBAL				
335	PIBAL				
300	AERO		215/6	240/7	

NOTES:
1. WIND ARROWS POINT DOWNWIND TO INDICATE DIRECTION OF EFFLUENT TRAVEL. COMPASS ORIENTATION IS CONVENTIONAL-CLOCKWISE FROM NORTH TO TOP.
2. PIBAL WIND VELOCITIES ARE BASED ON THEORETICAL RISE RATE OF A DRY, 30 gm PIBAL WITH 71 gms FREE LIFT.
3. THE AEROVANE WAS MOUNTED ABOUT 100 FT ABOVE GROUND ON A 200 FT HILL ONE-HALF MILE SE OF KEYSTONE.
4. PITTSBURGH RAWINSONDES FOR THE 2000 AND 3000 MSL LEVELS ARE PLOTTED AT SAME HEIGHTS ABOVE SURFACE AS AT PITTSBURGH.

Figure A.37 Wind Profiles, Run 21

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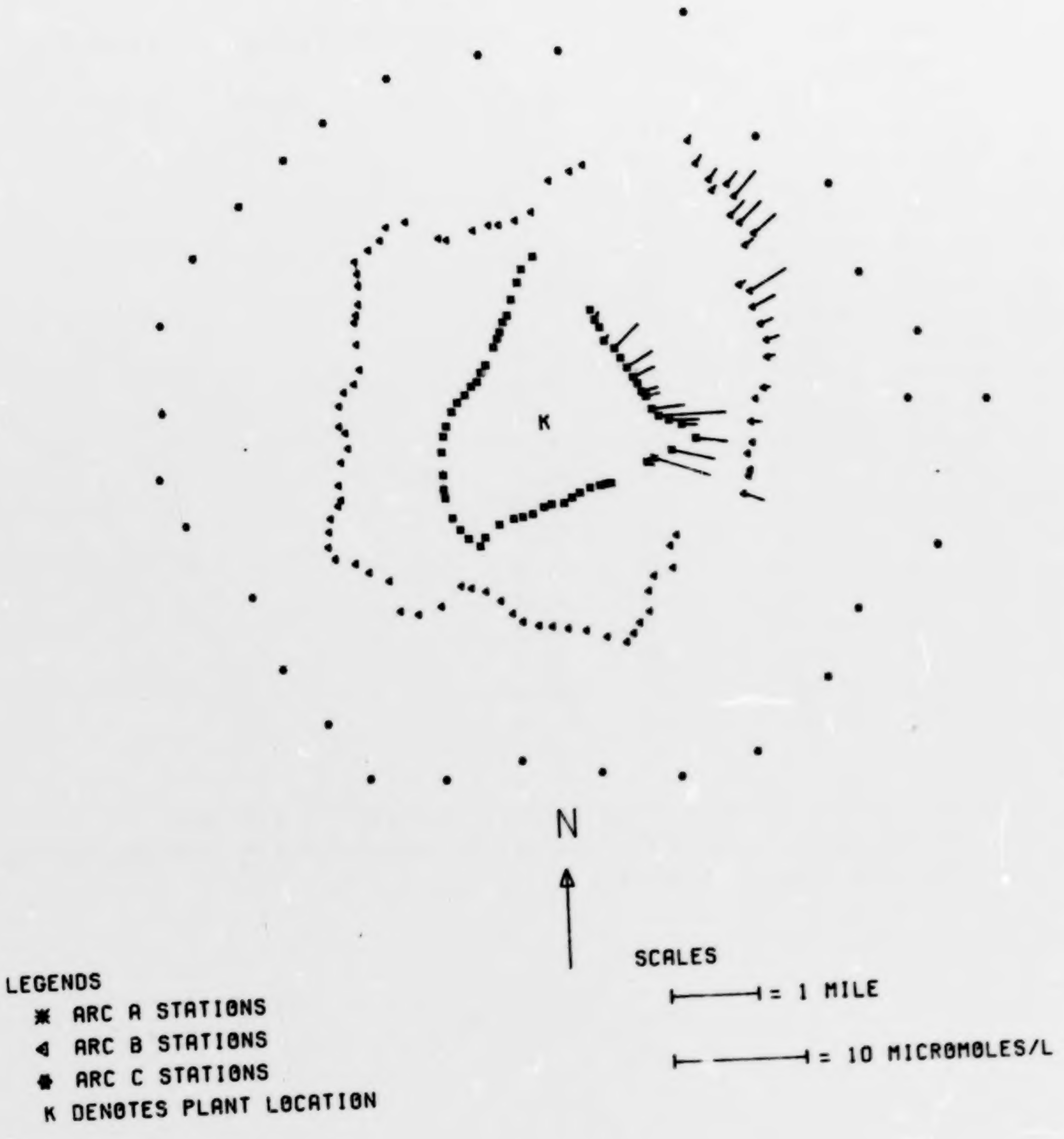
K
N
LEGENDS
✱ ARC A STATIONS
◀ ARC B STATIONS
● ARC C STATIONS
K DENOTES PLANT LOCATION
SCALES
= 1 MILE
= 10 MICROMOLES/L

Figure A.38 Sulfur Dioxide Distribution, Run 21

TABLE A.35

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 21 APRIL 29, 1970 ARC A

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
.0	10:29	14:40	.0	.8				
1.0	10:30	14:45	.0	.0				
2.0	10:31	14:47	.0	.7				
3.0	10:32	14:49	.0	.1				
4.0	10:33	14:50	.0	.6				
5.0	10:35	14:52	.0	2.6				
6.0	10:36	14:54	.0	.3				
7.0	10:37	14:56	.0	2.3				
8.0	10:38	14:57	.0	1.8				
9.0	10:41	14:58	.0	.1				
10.0	10:48	15:00	.0	1.3				
11.0	10:30	14:45	.0	1.1				
12.0	10:31	14:46	.0	2.5				
13.0	10:33	14:48	.0	5.1				
14.0	10:34	14:50	.0	2.3				
15.0	10:35	14:51	.0	1.2				
17.0	10:37	14:53	.0	2.4				
18.0	10:39	14:55	.0	3.3				
19.0	10:41	14:57	.0	4.4				
20.0	10:42	14:59	.0	.6				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.36

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 21 APRIL 29, 1976 ARC B

STA.	SAMPLING PERIOD		PRECIP VOLUME	CONCENTRATIONS IN SAMPLES				
	FROM	TO		SO2	SO4	NO2	NO3	PH
1.0	10:32	14:45	.0	.8				
2.0	10:34	14:48	.0	1.0				
3.0	10:36	14:51	.0	.5				
4.0	10:38	14:53	.0	1.2				
5.0	10:39	14:57	.0	2.5				
6.0	10:40	15:00	.0	1.5				
7.0	10:44	15:02	.0	2.3				
8.0	10:45	15:04	.0	2.2				
9.0	10:47	15:06	.0	.8				
10.0	10:51	15:09	.0	.6				
11.0	11:15	15:11	.0	3.2				
12.0	10:30	15:13	.0	1.9				
13.0	10:31	14:45	.0	1.0				
14.0	10:33	14:47	.0	1.0				
15.0	10:34	14:49	.0	.6				
16.0	10:36	14:51	.0	.5				
17.0	10:37	14:53	.0	.1				
18.0	10:38	14:54	.0	.8				
19.0	10:40	14:56	.0	.1				
20.0	10:42	14:58	.0	.1				
22.0	10:43	15:00	.0	.1				
23.0	10:45	15:02	.0	1.6				
94.0	10:30	15:04	.0	.5				

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

TABLE A.37

PRECIPITATION SCAVENGING DATA -- KEYSTONE STUDY

RUN 22 MAY 2, 1970 ARC B

STA.	SAMPLING PERIOD FROM	TO	PRECIP VOLUME	CONCENTRATIONS IN SAMPLES SO2	SO4	NO2	NO3	PH
19.0	15:00	18:33	91.0	.2				
21.0	15:03	18:38	106.0	.3				
23.0	15:06	18:40	116.0	.3				
24.0	15:08	18:43	116.0	.6				
25.0	15:10	18:45	114.0	.3				3.51
26.0	15:12	18:48	100.0	.3				
27.0	15:13	18:50	104.0	.4				
29.0	15:16	18:52	96.0	.3				
31.0	15:18	18:55	113.0	.4				
73.0	15:36	19:12	206.0	.3				3.76

NOTE: VOLUME UNIT IS ML. SO2 CONCENTRATION UNITS ARE MICROMOLES/L. SULFATE, NITRITE AND NITRATE CONCENTRATION UNITS ARE MILLIGRAMS/L.

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APPENDIX B

REVERSIBLE WASHOUT -- AN EXAMINATION OF THE CONSEQUENCES OF LINEARITY, NONLINEARITY, AND WASHOUT THROUGH DROPLET CAPTURE

Chapter III emphasizes the distinction between processes of reversible and irreversible washout. Additional examination of the equations demonstrates the utility of dividing the study of reversible washout into the two following subcatagories: linear and nonlinear. Linear washout processes are ones that satisfy the following requirement:

$$N_{Ao} = - K_y (y_{Ab} - Hx_{Ab}) \; ; \quad K_y \, , H \text{ constant} \quad , \qquad (B.1)$$

(cf. Equation 3.5). Nonlinear systems, conversely, are ones that do not satisfy Equation B.1. One should note here that "first-order" systems are not necessarily linear, unless Henry's law is obeyed.

The distinction between linear and nonlinear washout is somewhat artificial, since no washout process can be expected to conform exactly to the conditions of linearity. Some systems should approach linearity to a fairly high degree, however, and the use of this idealization is reasonably valid. Because of its blatant disobeyance of Henry's law the sulfur dioxide-water system must be considered nonlinear for most cases wherein washout is of interest; however, linear theory is still useful to some extent here, as will be shown in the following development.

To illustrate the properties associated with linear and nonlinear washout it is convenient to visualize a single drop of radius a falling through polluted air of concentration y_{Ab}. Performing a material balance on the drop and combining with Equation B.1 provides

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$$\frac{dc_{Ab}}{dz} = \frac{3K_y}{v_t a} (y_{Ab} - H' c_{Ab}) \quad , \qquad (B.2)$$

where c_{Ab} is the average concentration of pollutant in the drop and H' is the Henry's-law constant modified to units of c_{Ab}. For the corresponding case wherein Henry's law is not obeyed one may write

$$\frac{dc_{Ab}}{dz} = \frac{3K_y}{v_t a} (y_{Ab} - g' (c_{Ab})) \quad , \qquad (B.3)$$

g' denoting the appropriate nonlinear functional equilibrium relationship for y_{Ae} in terms of c_{Ab}.

Now consider a number of drops of radius a falling steadily through a stationary pollutant plume into a fixed collector at ground level. The plume concentration at any point (x,y,z) in space will fluctuate with time; however, the average concentration at that point may be expressed by the integral

$$y_{Avg} (x,y,z) \rightarrow \frac{1}{\tau} \int_{o}^{\tau} y_{Ab}(x,y,z,t)\, dt \quad , \qquad (B.4)$$

where τ is some appropriately-large averaging period.

For linear conditions Equation B.2 may be solved to obtain the ground-level concentration of any given drop

$$c_{Ao} = \frac{3K_y}{v_t a} \int_{z_o}^{o} \exp\left(\frac{3K_y z}{v_t a}\right) y_{Ab}\, dz \quad , \qquad (B.5)$$

where z_o is some datum point high above the plume. Since the plume is fluctuating with time, drops entering the collector at different times will have varying concentrations. The average concentration of steadily falling drops of radius a collected at times between t=o and t=τ is given by

$$c_{Avg} = \frac{1}{\tau} \int_o^\tau c_{Ao}(t)\, dt$$

$$= \frac{3K_y}{\tau a v_t} \int_{z_o}^{o} \exp\left(\frac{3K_y z}{v_t a}\right) \int_o^\tau y_{Ab}\, dt\, dz$$

$$= \frac{3K_y}{a v_t} \int_{z_o}^{o} \exp\left(\frac{3K_y z}{v_t a}\right) y_{Avg}\, dz \quad , \qquad (B.6)$$

showing that the time-averaged concentration in the collected sample should be related simply to the time-averaged concentration in the plume, whenever linear conditions prevail.

This same type of analysis can be applied to irreversible linear washout theory to produce a similar result. For nonlinear systems, however, analytical integration of Equations B.2 or B.3 (if possible at all) tends to weight disproportionately the influence of gas-phase fluctuations. Therefore, c_{Avg} cannot be expressed simply in terms of y_{Avg}; because of this much more must be known about the plume before washout can be determined, and the overall problem is complicated enormously.

It should be noted that this analysis is somewhat incomplete in that it implies that all drops of radius a that enter the collector have fallen through the same trajectory - a situation not expected to occur in nature owing to time-fluctuations in wind velocity. Further analysis of this question and of the consequences of employing average plume concentrations to nonlinear washout problems will be the subject of a forthcoming publication(68).

An extended analysis of Equation B.2 can be employed to investigate the significance of the mechanism of gas washout through pickup of suspended, gas-laden fog droplets. (Mechanisms 2-3-4-10 in Figure 1.1.) If one assumes (conservatively) that the rate of water-mass pickup by the falling drop is negligible compared to the mass of the drop itself, then from aerosol-washout theory(53) one may write

Gain of concentration in drop through mechanism 2-3-4-10 with

$$\text{distance} = \left.\frac{dc_{Ab}}{dz}\right|_{2\text{-}3\text{-}4\text{-}10} \cong -\frac{3E(a)\ m\ \rho_w\ y_{Ab}}{4\ a\ H'} , \qquad (B.7)$$

where m is the mass concentration of saturated, suspended, droplets, E(a) is the droplet washout efficiency, and ρ_w is the density of water. Assuming additivity of mechanisms, this may be combined with Equation B.2 to give

$$\frac{dc_{Ab}}{dz} = \left[-\frac{3E(a)\ m\ \rho_w}{4\ a\ H'} + \frac{3K_y}{v_z a} \right] y_{Ab} - \frac{3K_y\ H'}{v_z a}\ c_{Ab} \qquad (B.8)$$

which becomes, upon integration,

$$c_{Ao} = \left[- \frac{3E(a)\ m\ \rho_w}{4\ a\ H'} + \frac{3K_y}{v_z a} \right] \int_{z_o}^{o} \exp\left(\frac{3K_y\ Z}{v_z a} \right) y_{Ab}\ dz \quad . \qquad (B.9)$$

Inspection of Equation B.9 shows that the terms for pollutant-gas washout from the mechanisms of fog-droplet capture and simple gas absorption are additive; their relative effects, therefore, can be assessed simply by comparing the bracketted terms. Even though Equation B.9 pertains strictly to linear systems only, this equation can be utilized for order-of-magnitude comparisons for nonlinear washout simply by substituting constant equilibrium and mass-transfer coefficient values corresponding to the conditions of interest.

It is of interest to perform such a comparison for the sulfur dioxide-water system. Consider, for instance, a point in a plume wherein the ambient sulfur dioxide concentration is 0.5 parts per million, corresponding to a linearized H' of about 600 cm^3/mole. The following table provides a comparison of the relative importances of the mechanisms for drops of various sizes falling through this point. These calculations are based on the following values: $E(a) = 1$, $m = 3$ gm/m^3, K_y given by lowest values appearing in Table 3.2.

TABLE B.1

COMPARISON OF SULFUR DIOXIDE WASHOUT MECHANISMS

Drop Diameter, cm	$\frac{3E(a)\ m\ \rho_w}{4\ a\ H'}$ moles/cm^4	$-\frac{3K_y}{v_z a}$ moles/cm^4
0.03	2.5×10^{-7}	4.2×10^{-4}
0.10	7.5×10^{-8}	1.5×10^{-5}
0.30	2.5×10^{-8}	9.0×10^{-7}

From Table B.1 it is obvious that the fog-capture mechanism should never be a significant factor in sulfur dioxide washout by rain under these conditions. This is especially apparent when one notes that the values employed in calculating the groups in the table were chosen so as to accentuate, as much as is realistically possible, the relative effect of the fog-capture mechanism. One should note that at lower ambient concentrations of sulfur dioxide, the relative effect of the fog-capture mechanism should be enhanced, this arising from a lowering of H'. This enhancement, however, is still insufficient to render the fog-capture mechanism of any importance under circumstances of practical interest.

APPENDIX C

SIGN-X ANALYZER CALIBRATION

Laboratory calibrations of the Sign-X analyzer were performed using sulfur dioxide from permeation-tube and syringe-pump sources as shown in Figure C.1. Pure nitrogen was used as the diluent in all calibrations. Carbon dioxide was admitted to the system directly from a gas cylinder and controlled with a fine needle value. The results are given in Table C.1.

TABLE C.1

SIGN-X ANALYZER CALIBRATION

0 ppm CO_2 Added		256 ppm CO_2 Added	
SO_2 Concentration (ppm)	Sign-X Reading[*] (mv scale/10)	SO_2 Concentration (ppm)	Sign-X Readings[*] (mv scale/10)
0.110	0.077	0.000	0.053
0.143	0.097	0.118	0.131
0.147	0.100	0.143	0.159
0.198	0.143	0.146	0.160
0.202	0.145	0.180	0.182
0.250	0.181	0.191	0.193
0.252	0.195	0.235	0.227
0.368	0.300	0.265	0.237
0.419	0.361	0.306	0.278
0.580	0.430	0.383	0.345
0.910	0.610	0.594	0.476
0.945	0.735	0.925	0.760
2.00	1.09	2.00	0.985
4.00	2.30	2.00	1.09
8.00	4.26	4.00	2.06
		8.00	3.99
		8.00	4.15

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[*] Corrected for zero and reagent conductivity, read as minimum value of fluctuating curve, filter out.

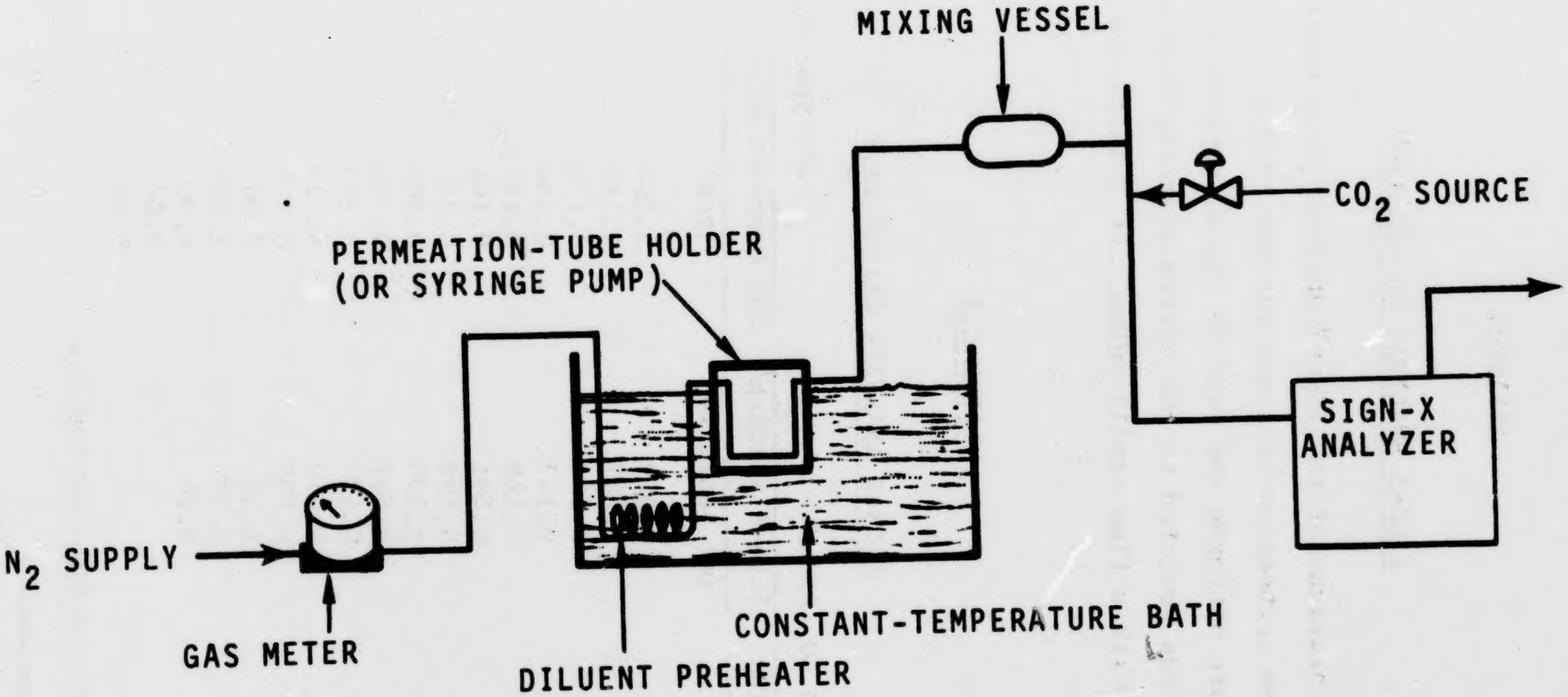
MIXING VESSEL
CO_2 SOURCE
PERMEATION-TUBE HOLDER (OR SYRINGE PUMP)
SIGN-X ANALYZER
N_2 SUPPLY
GAS METER
CONSTANT-TEMPERATURE BATH
DILUENT PREHEATER

Figure C.1 Schematic of Calibration Equipment